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EXPLOSIVE COMPOSITIONS

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Abstract

1. Arrangements have been made to manufacture 5000# of PEP-2 at the duPont Eastern Laboratory.

Samples of PEP-2 continue to show no appreciable changes in plastic properties after 5-1/2 months' storage at 60°C.

Polar RDX PE made with British lecithin continues after 2 months' storage at 60°C. to retain its plasticity. Under similar storage conditions plastic made with American soy-bean lecithin has badly deteriorated in consistency.

In the flame sensitivity test, it has been found that Tetryl-IPE has a rather high inflammability index (I.I.), and that RDX-IPE has a higher I.I. than Polar RDX PE. On the other hand, PETN-IPE, like PEP-2, cannot even be burned in this test.

Tests with the cal. 0.50 ball ammunition have shown that RDX and PETN-IPE's are definitely less bullet-sensitive than Composition C-2 and PEP-2.

2. Further bullet tests have confirmed the reduction in sensitivity of Composition B produced by increasing its wax content to 4%.

3. The relative insensitivity of the liquid explosive Methylite-20* has been further demonstrated by its ability to withstand without detonation the blow of a 125 lb. hammer falling through 5 ft., and crushing a half-pint can of the explosive on a steel plate.

4. Further attempts to initiate thin films of Torpex between metal surfaces have given no detonations capable of propagating to attached large charges.

A further study of the contact angle made by the TNT-Wax (Aristowax-Alox) interface on aluminum has been made, with special reference to the hysteresis of the contact angle. It has been found that aluminum particles cannot be completely covered by this wax in the presence of molten TNT.

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* A liquid explosive mixture developed at the ERL, consisting of 80% Nitroglycerine (NG) and 20% dimethylphthalate (DMP). The Nitroglycerine contains 25-30% of diglycerine tetranitrate (DGTN) as an anti-freezing agent.

5. Further experiments with quaternary ammonium salts as agents to improve the pourability of Ednatols have verified the fact that they are effective. The particular salts used, however, decompose slowly in the slurry at 100°C, so search is being made for more stable salts.

It has been found that the acetone-extract of commercial lecithins is a very good agent for improving the pourability of Ednatols, and does remain stable. The constituent of the mixture which is active has not been identified.

1. Plastic Explosives

(1) PEP-2

Arrangements have been made for the shipment of 2500 paper boxes, 2750 sheets of vegetable parchment paper, and two drums of Crown E oil, to the duPont Eastern Laboratory for the manufacture of 5000 pounds of PEP-2.

(2) Storage Tests.

(a) PEP-2.

All of the samples of PEP-2 in various wrappings have been in 60°C storage for 5-1/2 months and still show no appreciable change in plastic properties.

(b) RDX Polar P.E. made with British lecithin.

After 2 months' storage at 60°C in closed and open containers, the sample of RDX Polar PE made with British lecithin still shows no sign of deterioration. It has become firmer, but there is no evidence of surface cracking, as was seen after similar storage in samples of similar plastic made with American soy-bean lecithin. This further confirms the difference in behavior of the British lecithin from Arachis nuts and the American soy bean product, with respect to storage stability of the RDX Polar plastic, reported in last month's report (PT-18, p.5).

(3) Insensitive Plastics.

No further developmental work has been done on insensitive plastics (designated RDX-IPE or PETN-IPE). Further exudation tests of the mixtures described in Division 8 Interim Report PT-17, p.5, are being carried out by the following method, which it is hoped will be more realistic than the standard method hitherto employed for plastics. A steel cylinder 1-1/2" I.D. by 1-5/8" O.D. is filled with the plastic and suspended over a watch glass which will catch any oil that drips out.

After various times of storage at 60°C, the oil which has dripped out will be weighed, and, in addition, portions of the plastic will be analyzed for oil to determine any changes in concentration over the length of the sample.

Since the results of the standard exudation test were so high, attempts are being made to cut down the loss of oil. In one such attempt, very fine PETN, made by drowning an acetone solution of PETN in water was used. This material was too fine to give a plastic with 19% oil, but it is felt that a reduction of exudation may be effected by controlling the particle size.

Other methods of reducing exudation, such as the bodying of the oil by the addition of soaps, are under consideration and will be explored.

Some time has been spent preparing large batches of PETN-IPE, RDX-IPE and Tetryl-IPE for rifle testing with incendiary ammunition.

(a) **Flame Sensitivity.**

The Inflammability Indices (see "Physical Testing", this report, Page 16) of seven plastic explosives have now been determined. The insensitivities to flame of the insensitive plastics are of special interest in the following table.

Explosive	Inflammability Index
PETN-IPE	0 (will not burn)
PEP-2	0 (will not burn)
duPont PETN-Gelatin	50
RDX Polar PE	138
RDX-IPE	162
COMPOSITION C-2	178
Tetryl IPE	195
Composition C-2'	229

Contrary to what might be expected, the RDX-IPE is more sensitive than the RDX Polar PE. This may merely be due to the presence of bare crystals on the surface of the unrolled RDX-IPE. These crystals are not protected by a film of oil, and therefore may be ignited more readily. That this is reasonable is possibly also indicated by the fact that the unrolled Composition C-2' has a higher Inflammability Index than the rolled Composition C-2, which is otherwise of rather similar composition.

The Tetryl-IPE behaves a little differently from the other plastics, its reaction being more like that of a cast explosive than that of a plastic. In most instances, the material starts burning, but continues to burn for only 15-20 seconds. Such a reaction is not counted as a burning in determining the Inflammability Index.

(b) Bullet Sensitivity (W.H. Rogers)

Since even the ordinary RDX plastics, such as Composition C and Composition C-2, and PEP-2 are insensitive to cal. 0.30 ball ammunition, an attempt to distinguish their sensitivities from those of the RDX and PETN insensitive plastics has been made, using cal. 0.50 ball ammunition. The plastic samples were contained in 2" pipe-nipple containers. The following results have been obtained.

	NE	EP	E	EC
Composition C-2	10/4	5	1	--
PEP-2	9/4	5	-	--
RDX-IPE	10/10	-	-	--
PETN-IPE	10/10	-	-	--

This test shows clearly that the "insensitive plastics" are less bullet-sensitive under these conditions than the ordinary ones. It is planned to supplement these tests with tests of all the important plastics, using 0.30 and 0.50 caliber incendiary bullets.

2. Composition B.

(1) The Use of Paraffin in Composition B. -(L. Goodman)

Standard exudation tests have been made to compare the amount of wax exuded at 60°C from Composition B samples made with paraffin with the amount exuded by commercial samples made with Aristowax-Alox. The results were rather irregular and are being repeated.

Bullet sensitivity tests of this type of Composition B, using caliber 0.50 ball ammunition, are under way.

(2) "Superwaxed" Composition B. (O. Bolduan and W.H. Rogers).

A Composition B whose composition was 60/40/3.8/0.2, RDX/TNT/Paraffin/Lecithin, has been tested in the 1" pipe nipple assembly with cal. 0.30 ball ammunition, and gave 2 failures in 20 trials (PT-18, p.9). In an effort to increase the precision of this sensitivity determination and, at the same time, be sure the failures were independent of the preparation, 20 more samples were made up and the containers numbered in the order of pouring. Samples 1-9 were poured at about 90-95°C while 10-20 were poured at 85-90°C. In this series there was one failure (#12). The results of all tests on this composition are: -

	NE	EP	E	EC
40	37	2	1	--

These results suggest that this material has been greatly desensitized by the extra wax. However, it is almost too insensitive to be well tested with the cal. 0.30 bullet test. Samples are to be tested using the more appropriate cal. 0.50 bullet.

3. Liquid Explosives. (L. Goodman)

T o supplement earlier measures of the insensitivity of Methylite-20, a 125 lb. pendulum-hammer was dropped from a height of 5 ft. onto a half-pint paint can filled with the liquid explosive. The can was completely smashed by the blow, but there was no evidence of detonation.

4. Torpex.

(1) Sensitivity and Propagation of thin layers of Torpex.

(L. Goodman)

Attempts have been made to detonate wedge-shaped Torpex charges by impact of a cal. 0.50 machine gun bullet. The charge used was cased in 1/32" steel and had a thin portion which had the approximate dimensions 2" x 1" with about 2-4 mm. thickness of Torpex. The top of the charge was flared out to give a 3" x 2" x 1" block of Torpex. This charge was fastened to a 3/4" steel back plate and struck in the thin portion with a cal. 0.50 ball bullet, with no further cover plate than the 1/32" case. In two trials no detonations were observed. Our experience with large charges of Torpex indicates that a thick layer of this explosive, so cased and struck with such a bullet, would in general detonate at least low order.

Some experiments have been carried out to determine whether a block of Torpex connected by a thin layer of Torpex to a second block of explosive is detonated by sympathetic detonation or by propagation through the thin layer when one of the blocks is set off, high order, by a detonator-booster assembly. When two blocks, connected by a layer of Torpex about 2 mm. thick, 3" wide and 6" long, have several steel plates protecting the second block from the first, detonation seems not to be transmitted to the second through the thin layer. Similar experiments are being made to determine the thickness of layer required to transmit the detonation for a distance of 6".

(2) The Wetting of Aluminum in TNT by Wax. (O. Bolduan)

The contact angles of TNT and of Beeswax on aluminum have been measured (PT-15, p.10) and a description of the physical state of the wax and aluminum particles in Torpex has been given (PT-14, p.10). Values for the actual interfacial contact angle, TNT-Wax on aluminum, has not been previously given, and until this has been determined to be greater than zero on the wax side under both advancing and receding conditions, the possibility of aluminum particles being completely covered by wax, even in the presence of TNT, cannot be completely ruled out. This interfacial contact angle has accordingly been measured, using Aristowax-Alox as the wax.

A plate of polished aluminum was placed in a bath of Aristowax-Alox (10% Alox). Droplets of TNT were dropped onto it. The shape of the droplets was observed. The droplets were found to have a contact angle which was slightly less than 90° on the wax side.

The reverse of this condition was observed. A plate of aluminum was suspended horizontally in a bath of molten TNT. Droplets of wax were placed underneath the aluminum. The droplets were observed to have a contact angle slightly less than 90° on the wax side. The aluminum was shaken vigorously and allowed to stand for a half-hour. The droplet flattened only slightly but there was no tendency to spread. Accordingly, neither the advancing nor receding contact angles are zero on the wax side. Therefore, aluminum cannot be completely covered with a layer of wax in the presence of molten TNT.

5. The Effect of Surface-active Agents on the Pourability of Ednatols. (O. Bolduan)

(1) Quaternary Ammonium Salts.

Further studies of the use of two quarternary ammonium salts, dimethyl benzyl stearyl ammonium chloride and lauryl pyridinium bromide (PT-18, p.13) indicate that the reported darkening of Ednatol slurries in their presence was due in part to the fact that the early experiments were performed in copper beakers. In stainless steel the discoloration is much reduced but still present. The visible improvement of the viscosity of Ednatol slurries by such agents has, moreover, been confirmed by repeated tests.

It was suggested that the darkening of the slurries is probably the result of decomposition of the quaternary ammonium salts, and subsequent reaction of their decomposition products with TNT. In particular, it was pointed out that the benzyl group might contribute to the instability of dimethyl benzyl stearyl ammonium chloride. Samples of other quaternary ammonium salts are being obtained and prepared in a search for one which will be more stable in the presence of TNT.

(2) Lecithin.

It has been found that the addition of a thin oil, found at the top of a can of soy-bean lecithin (Hachmeister), improves the pourability of Ednatol slurries greatly, and does not cause discoloration or deterioration of the behavior of the product in the 135°C thermal stability or 100°C vacuum stability tests. However, it was found that the addition of this lecithin thoroughly mixed, or of the thick fraction of this lecithin did not improve the pourability, but decreased it, in most cases, until the resulting slurries were worse than those with no additive. The addition of this thick fraction caused a change in the texture of the slurry such that it resembled more closely the texture of a slurry to which the thin oil fraction had been added, but large aggregates were formed and the slurry became more "doughy". Other single-phase lecithin samples behaved in general like the thick fraction of the Hachmeister sample, and did not improve pourability.

Accordingly, three different lecithin samples were separated by acetone extraction into two fractions. The acetone residue consists mainly of lecithin and kephalin, while the acetone extract contains most of the other constituents of the crude lecithin. An approximate analysis gave:

Sample	% Acetone Extract
a) Soy-bean lecithin (Hachmeister)	46
b) Soy-bean lecithin (Bergstrom)	29
c) Arachis nut lecithin - British (J.Bibby & Sons)	26

It was found that the acetone extracts from each of these samples improved the pourability of 56/44 Ednatol slurries, while the acetone residues made their pourabilities worse.

The active ingredient in this acetone extract is, as yet, unknown. Some of the possibilities are:

(1) Lecithin - This is insoluble in acetone but is more soluble in the presence of fats. Partially purified lecithin decreased the pourability.

(2) Triglycerides - soya bean oil which is mainly a triglyceride was tried. No effect on the pourability.

(3) Fatty Acids - all lecithins have at least one unsaturated fatty acid and usually oleic or linoleic acid. Oleic acid had no effect on the pourability.

(4) Mono - or diglycerides - A mixture of monoglycerides from cocoanut oil was tried. No effect on the pourability was observed.

Moreover, none of these, except lecithin, increased the pourability of a slurry consisting of Haleite in nitrobenzene or benzene. Lecithin did aid these slurries, though it does not aid the slurry in TNT.

The behavior of lecithin in molten TNT was observed. Lecithin which had been extracted with acetone was added to molten TNT. It formed a hard mass, appeared somewhat decomposed and showed no tendency to dissolve. This suggested the possibility that a good dispersion of the lecithin is necessary for its action. To test this hypothesis, lecithin was dissolved in benzene, Haleite added, filtered off and dried. This lecithin-coated Haleite was added to molten TNT to form a 56% slurry. The resulting slurry was poorer than one with no agent and darkened considerably upon standing. Some lecithin was also dissolved in paraffin oil and in soya bean oil and then added to a 56% slurry. No effect was observed.

Accordingly, it appears that there exists, in the acetone extract of commercial lecithins, one or more materials which are good surface-active agents for the improvement of the pourability of Ednatols.

PHYSICAL TESTING

Report Submitted by

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1. Impact and Mortar. R. Davis

During the four-week period between February 14 and March 11, 1944, 9977 shots were fired on 300 samples in the various impact machines. Most of the samples tested were of local interest. Some time has been spent on the "tooth-pick" design (Machine No. 13), in which the flat striker is suspended over the sample on the flat anvil by means of a splinter of wood, which breaks when the weight hits the striker. In this machine, the striker delivers a real blow to the sample without the spreading effect produced in the more conventional design when the striker is pressed against the sample preparatory to dropping the weight. This method has proven particularly useful in testing liquid explosives. As the results are still in a preliminary stage, no figures will be reported at this time, but a full report on this and the sandpaper design (Machine No. 12) will be given later.

2. Bullet Sensitivity Tests. W. H. Rogers

(1) Studies of the Effect of the Container on Bullet Sensitivity.

A series of experiments has been undertaken that has as its object the determination of the effect of the nature of the container - particularly its size - upon the sensitivity of an explosive to bullet impact. It is already known, of course, that very light containers such as cardboard or sheet metal give lower sensitivities than heavier containers such as pipe-nipples, but that when containers become so heavy that they are not perforated by the bullets, the sensitivity again decreases sharply. It would also appear, however, that large charges in such service containers as bombs and depth charges are more sensitive to bullet impact than the same explosives confined in small laboratory containers.

To study the effect of size on container, within the weight limits which our testing facilities permit, pipe nipple containers of various sizes have been chosen. To keep down the weights, the lower cap has been filled with paraffin, while the upper one, as usual, has been left empty. Now as the diameters of the pipe-containers change, their wall-thicknesses change also, but generally this is also the case with munitions of a given type, so it does not seem to be a great disadvantage. Cast Pentolite (50/50) and perhaps also cast Composition B or 60/40 Cyclotol are to be used as typical ordinary explosives, while cast Torpex II will be used as a typical aluminized explosive.

(a) Effect of Length of Container.

The effect of increasing the length of the regular 1" pipe-nipple from 1-1/2" to 3" has been studied with cast Pentolite, and, more briefly, with cast 60/40 Cyclotol and Torpex II. In the latter two cases the data on 1-1/2" long nipples were not obtained with the lower cap wax-filled, so there may be some doubt about the validity of the comparisons, although with Pentolite the results seem very little changed by substituting wax for explosive in the caps. The following results have been obtained:

Pentolite, 50/50 Cast	No.	N.E.	E.P.	E.	E.C.
1" p.n., 1-1/2" long	20	6 (30%)	5 (25%)	6 (30%)	3 (15%)
1" p. n., 3" long	40	30 (75%)	3 (7.5%)	2 (5%)	5 (12.5%)
Cyclotol, 60/40, Cast					
1" p.n., 1-1/2" long	186	100 (54%)	57 (31%)	17 (9%)	12 (6%)
1" p.n., 3" long	10	9 (90%)	1 (10%)	- -	- -
Torpex II, Cast					
1" p.n., 1-1/2" long	34	9 (35%)	25 (65%)	-	-
1" p.n., 3" long	10	1 (10%)	7 (70%)	2 (20%)	-

With Pentolite, the decrease in sensitivity with length is reasonably well verified, and the results with Cyclotol seem in agreement. It is not at all clear that the increase in sensitivity indicated by the results with Torpex II is real, more work is to be done on this subject.

(b) Effect of Diameter of Container

The effect of increasing the diameter is to be studied with 3" long nipples of 1", 3" and 5" pipe, using the same explosives as in part (a). The following results have been obtained:

Pentolite, 50/50, cast	No.	N.E.	E.P.	E.	E.C.
1" p.n., 3" long	40	30 (75%)	3 (7.5%)	2 (5%)	5 (12.5%)
3" p.n., 3" long	19	7 (37%)	7* (37%)	4 (21%)	1 (5%)

* Three of these partials were merely flaring or burning.

With the 3" nipples there was no indication that the bullet reached the back wall of the container with any force. Examination of the used 3" containers showed that the bullet was broken up completely, and tended to spread its effect over a larger and larger region as it progressed through the ex plosive.

The 5" nipples are in preparation, and more work is scheduled with the 3" nipples, using Torpex II.

(2) Sensitivity of Plastic Explosives to Incendiary Bullets.

Sensitiveness to incendiary bullet impact is being investigated for plastic explosives. An assembly of 2" pipe nipples (empty) with both caps filled with PE is suspended so that the cal .30 incendiary bullet enters the empty pipe nipple and only the incandescent gases come in contact with the sample. This method of testing does not affect either PEP-2 or Composition C-2, in 5 trials.

	N.E.	E.P.	E.	E.C.
PEP-2	5/5			
Composition C-2	5/5			
Composition C (ERL)	4/3	one burning		

A more realistic test for determination of sensitivity to incendiary ammunition has been devised. A 3"x3"x3" box is filled with the plastic, and the open end is covered by a plate, sufficiently thick to set off vigorously the projectile.

Both cal. 0.30 and cal. 0.50 incendiary ammunition have been used on PEP-2. With cal. 0.50 ammunition, 2 fires have been observed on the ground, and there may have been a small flash in each case but damage to the containers was so light that it is believed no detonation occurred.

	N.E.	E.P.	E.	E.C.
Cal. 0.30 Incendiary Ammunition				
PEP-2 - 3"x3"x3" boxes - 3/16" front plate	10/10			
Cal. 0.50 Incendiary Bullet				
PEP-2 - 3"x3"x3" boxes - 1/4" front plate	10/8	2*		

*Burned on the ground.

Tetryl IPE will next be tested with incendiary ammunition to see whether more reaction will be evidenced, since Tetryl IPE, as determined by the flame-test, seems to be the most flame sensitive of all the plastics, with the exception of Composition C-2'. The tests will then be extended to include Composition C-2, Polar RDX PE, RDX-IPE and PETN-IPE.

(3) Routine Testing

During the month other bullet tests of a more routine nature have been made, some of which have been summarized in the appropriate sections of the Explosive Compositions division of this report. For completeness they are all summarized in the following table.

Explosive	Bullet	Loading	Container	Results No.	NE	EP	E	EC
Composition C-2	0.50 ball	Hand-packed	2" p.n.	10	4	5	1	-
PEP-2	0.50 ball	Hand-packed	2" p.n.	9	4	5	-	-
RDX-IPE	0.50 ball	Hand-packed	2" p.n.	10	10	-	-	-
PETN IPE	0.50 ball	Hand-packed	2" p.n.	10	10	-	-	-
Superwaxed Composition B	0.30 ball	Cast	1" p.n.	20	19	1	-	-
Minol II	0.30 ball	Cast	1" p.n.	10	--	10	-	-
Minol II	0.30 ball	Cast	3x3x3" boxes	10	8	2	-	-
75/25 Tetrytol	0.30 ball	Cast	3x3x3" boxes with 1/2" steel back plate	5	5	--	-	-

3. Flame Sensitivity of Explosives. C. A. Weltman

During the past month, work has been resumed on the measurement of sensitivity to flame of various plastic explosives, using the methods already described in Division 8 Interim Report PT-15, p. 16.

For this test, attempts to change the flame in order to bring more explosives on the scale of the machine have been abandoned. Instead, for explosives which are off the scale, a stop-watch is used to determine the exposure time necessary for ignition. The results from this method are not as good as those using the rotating wheel, but are sufficiently good to order the explosives which are off the scale. The results are expressed in terms of an Inflammability Index (I.I.) which is 100 divided by the average of the minimum time of exposure which will give 10 burnings out of 10 trials and the maximum time of exposure which will give 10 non-ignitions in 10 trials. The higher the I.I. the more sensitive the sample. The results on plastics follow.

Explosive	Max.Time (in sec.)=10 N.F.	Min.Time(in sec.)=10 F	Av.	I.I.
PEP-2		Will not burn.		
PETN-Gelatin	1 sec.	3	2	50
RDX-Polar PE	.643	.806	.725	138
RDX-IPE	.537	.697	.617	162
Composition C-2	.537	.589	.563	178
Tetryl-IPE	.384	.643	.514	195
Composition C-2[1]	.336	.537	.437	229

Only one cast explosive has been completely tested in this machine. Others will be tested as time permits.

Composition B I.I. = 177

THE EFFECT OF HEAT ON CONFINED EXPLOSIVES

Report Submitted by
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Investigation Group: E. C. Broge and H. A. Strecker

In connection with the phenomenon of "cooking off," the study of the effect of heat on confined explosives was continued. This investigation was begun at the request of the Naval Bureau of Ordnance with the aim of eliminating, or minimizing the effects of accidents due to loaded shells being allowed to remain in overheated guns. The apparatus being used and the first results obtained were described in Division 8 Interim Report PT-18.

The "explosion temperature" of various materials has been studied in small steel bombs equipped with two thermocouples. One is sealed into a 3/8" deep well in the bottom of the cylinder. This couple records the bomb temperature. The second thermocouple is led into the interior of the bomb through a hole in the pipe plug which closes the bomb. This couple records the temperature of the charge in the bomb. It is insulated, and the seal made gas tight with a plastic porcelain cement (Sauereisen Cement #30). The arrangement is the same as that described in PT-18 for experiments #77-81 with Tetryl as the charge material. A photograph of the bomb, showing the arrangement of the thermocouples, is shown in Figure 1.

The new data are given for each experiment in temperature-time graphs of the interior and exterior thermocouple readings. The data are also summarized in Table I. For each experiment an "explosion temperature" range is recorded in columns 7 and 8 of Table I. The lower limit of this range is defined as the temperature at which the heating rate of the charge (the interior couple) just exceeds that of the bomb. It is the temperature at which perceptible decomposition of the charge material begins. For the upper limit it was desired to pick a temperature at which the rate of decomposition of the sample was fairly rapid. This point has been arbitrarily picked as the temperature at which the heating rate of the charge is double that of the bomb. It is realized that these two temperatures can not be very accurately determined from the heating curves. However, they do allow a rough objective comparison to be made of the behavior of different explosives.

In column 9 of Table I is recorded the action of the charge on the containing bomb as an indication of the violence of the explosion. Several control experiments, in which 10 and 20 grams of Tetryl were detonated in the bombs resulted in their fragmentation into thirty or more pieces. On this basis, none of the explosions observed were true high order detonations. In column 10 of the table are recorded the melting points for the sample in question, obtained from OSRD Report #830. The values are to be compared with the breaks in the heating curves recorded in column 3 of the table. Discussion of each compound follows.

Tetryl - The heating curves for Tetryl were given in the previous report. (PT-18, page 18 ff.) For completeness, data on this material are included in Table I. Experiment #81 was made with a slower heating rate than usual. No effect on the explosion temperatures resulted from this change.

Ammonium picrate (Explosive D) - Decomposition apparently sets in very gradually for this material. The lower explosion temperature is poorly defined. The explosions were not violent. In each case the plug was blown out, while the cylinder itself was undamaged. Doubling the rate of heating has no effect on the results. Heating curves are shown in Figure 2.

Haleite (EDNA, ethylene dinitramine) - Explosion for this substance occurs soon after decomposition sets in. Two early experiments were made in which the bomb temperature only was recorded. Again, one experiment with a heating rate about double the others did not affect the explosion temperature. Results are given in Figure 3.

RDX (Cyclonite) - Two kinds of RDX were studied. The Bachmann material (R-1975) contains about 5% HMX (cyclotetramethylene tetranitramine) and shows a melting point break at 190°C., corresponding probably to the RDX-HMX eutectic temperature. Rapid decomposition sets in when this point is reached. Heating curves for RDX-B are shown in Figure 4.

Woolwich RDX (R-2106) contains little, if any, HMX. Four out of the five experiments showed a definite melting point hold in the temperature-time curve at about 202°C. This is in quite good agreement with the melting point reported for Woolwich RDX samples. However, decomposition becomes quite rapid before this point is reached, so that there is little practical difference in the behavior of the two materials. Heating curves are shown in Figure 5.

Because of the masking effect of the melting temperature for both the materials, the explosion temperature limits are indefinite. It appears, however, that little decomposition takes place before

190°C. for either of the samples. At this point the decomposition of the Bachmann RDX becomes within several degrees very rapid, while the decomposition of the Woolwich RDX does not become equally rapid until it reaches the melting point, about 202°C.

PETN - This material shows no thermal evidence of decomposition until the melting point is reached. At this point it is difficult to say whether the increased heating rate of the charge is due to decomposition, or to the temperature lag produced by the melting of the charge. The lower explosion temperature is thus around 140°; the upper limit is indefinite. Results are given in Figure 6.

TNT - The upper explosion temperature, the point at which decomposition becomes rapid, is fairly well defined. The lower temperature is indefinite. Decomposition sets in gradually over quite a range of temperature. Heating curves are shown in Figure 7.

It is evident from the temperature-time records that no one temperature can be chosen as the "explosion temperature" for a particular explosive. A series of experiments is being carried out with the object of determining the highest temperature at which the 10 or 20 gram charge can be held without exploding. The bomb is heated rapidly to a predetermined temperature, and the heater current then adjusted to hold it at that temperature. Two experiments of this kind have been completed with Tetryl as the charge material. In the first case 10 grams of Tetryl was held at 162 $\pm$ 3°C. for 82 minutes. No explosion occurred, but it was evident that slow decomposition was taking place both from the tarry appearance of the residue in the cylinder at the completion of the experiment and from the fact that the internal temperature of the cylinder remained about 5° above the external temperature during the period of heating. The second 10 gram sample was held at 164 $\pm$ 4°C. for 280 minutes. After this period of constant temperature, the cylinder was heated until at 305°C. a very mild "explosion" occurred, resulting in no damage to the cylinder or plug. Apparently the residue of sample remaining after the prolonged period at 164°C. was less sensitive to further heating than the original Tetryl, which explodes reproducibly at about 175°C.

In preparation for future experiments on the effect of heat on 5" Naval shells, it was necessary to find an inert substance which had about the same thermal conductivity when loosely packed as ammonium picrate at density 1.5. Measurements of the thermal gradient at different rates of heating for various substances, including ammonium picrate, were made with two thermocouples placed a constant distance apart. It was found that a 75/25 sodium acetate/sodium chloride mixture had the desired thermal conductivity.

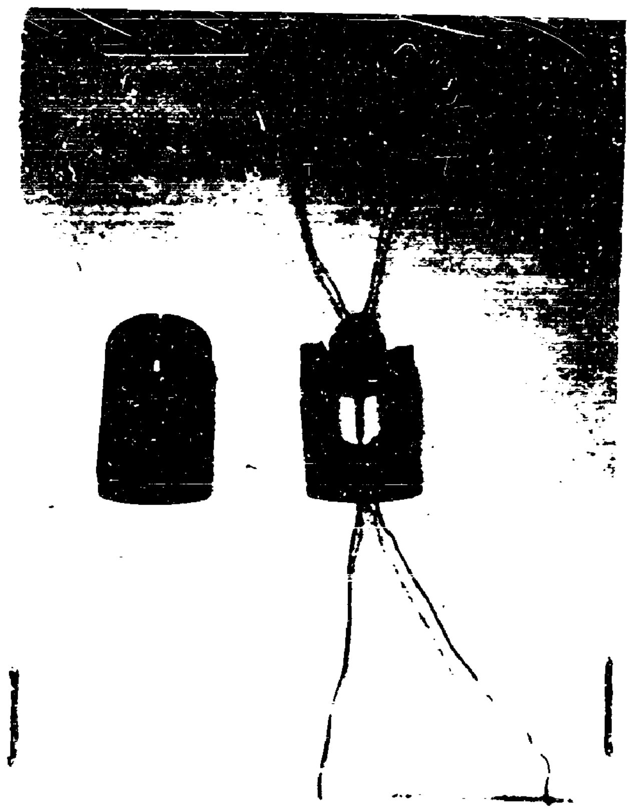
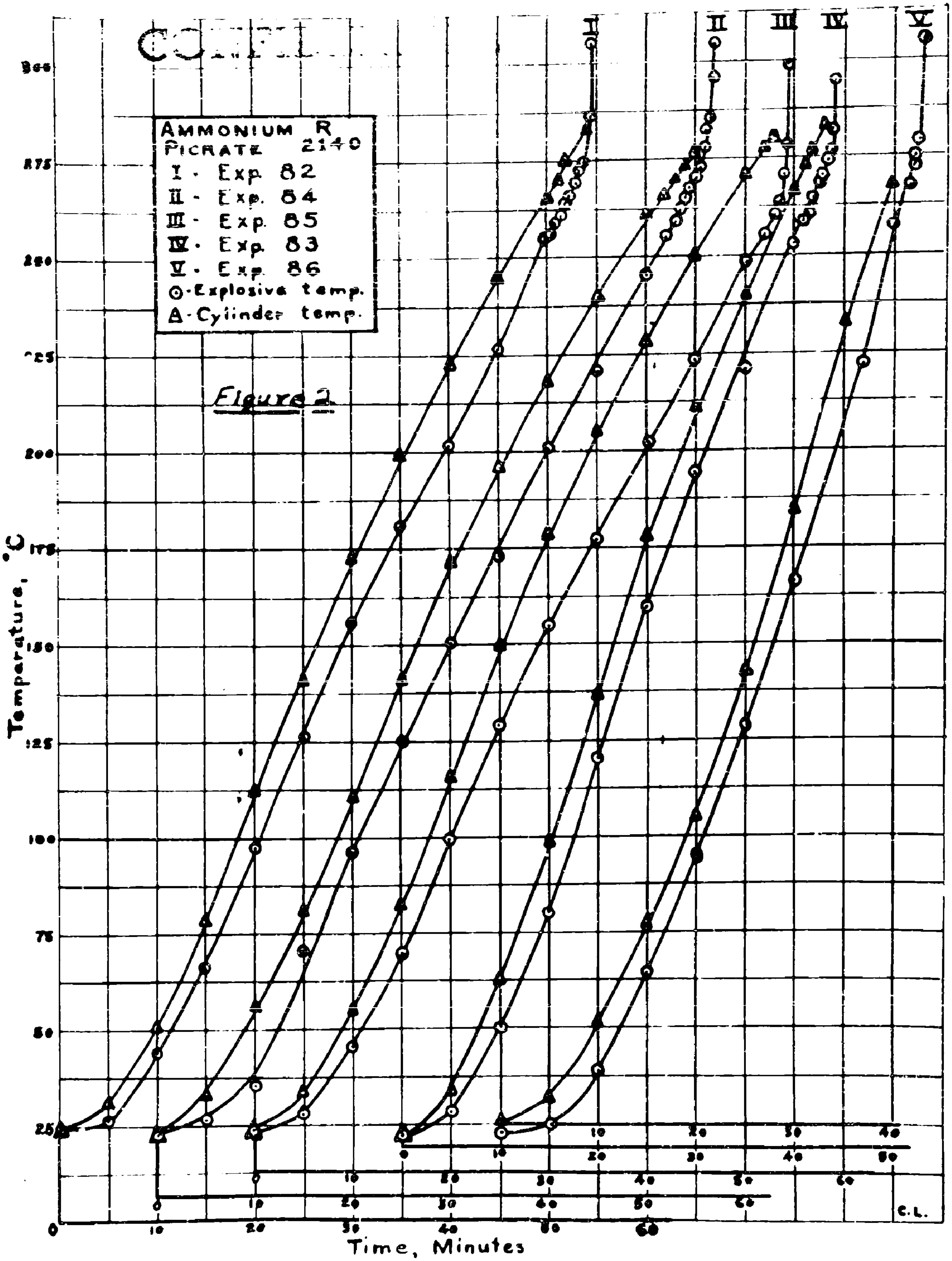
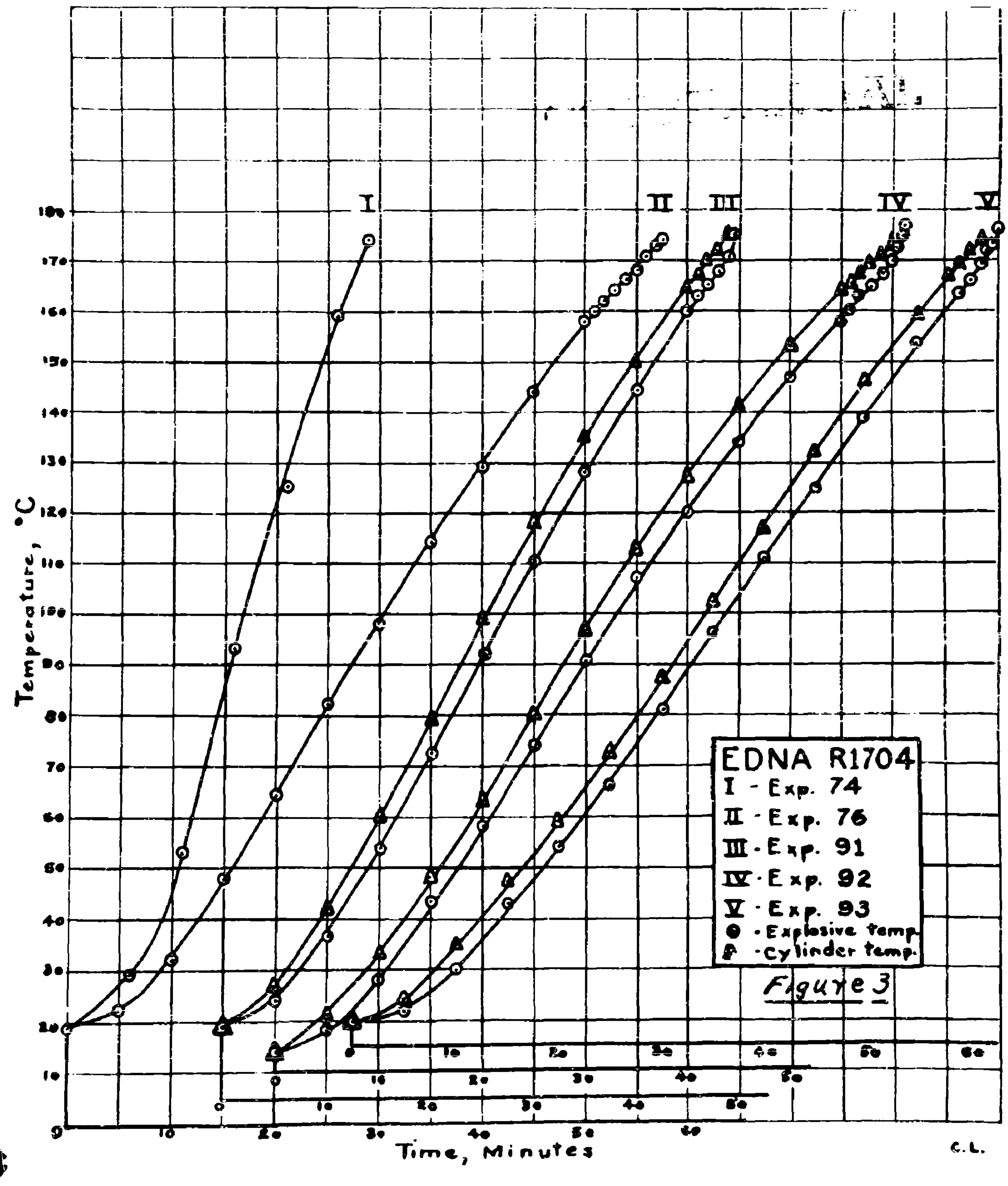


Figure 1

Cylinder and section, showing thermocouple arrangement.

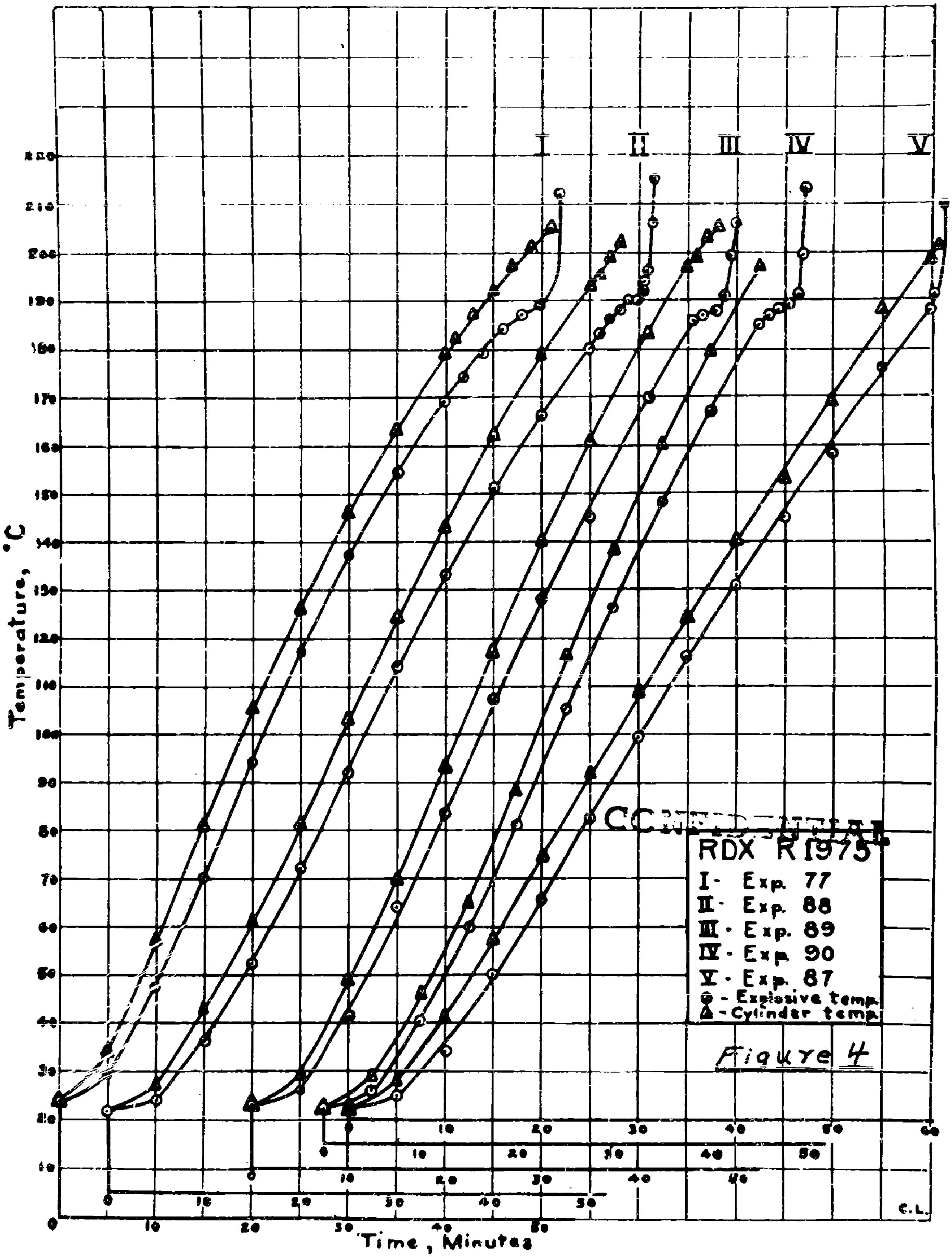


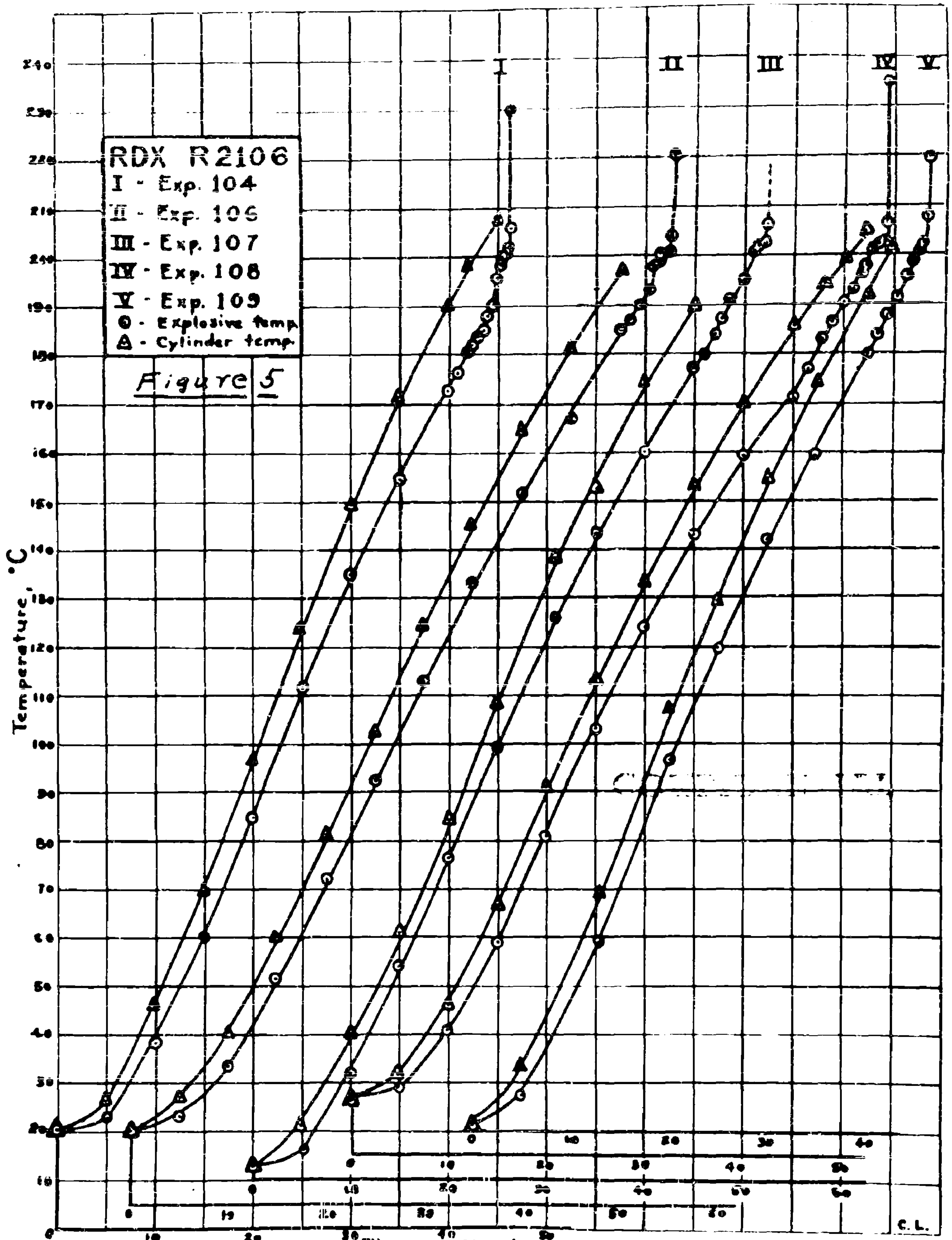
AMMONIUM PICRATE
R 2140
I - Exp. 82
II - Exp. 84
III - Exp. 85
IV - Exp. 83
V - Exp. 86
⊙ - Explosive temp.
Δ - Cylinder temp.
Figure 2
I
II
III
IV
V
Temperature, °C
Time, Minutes
C.L.



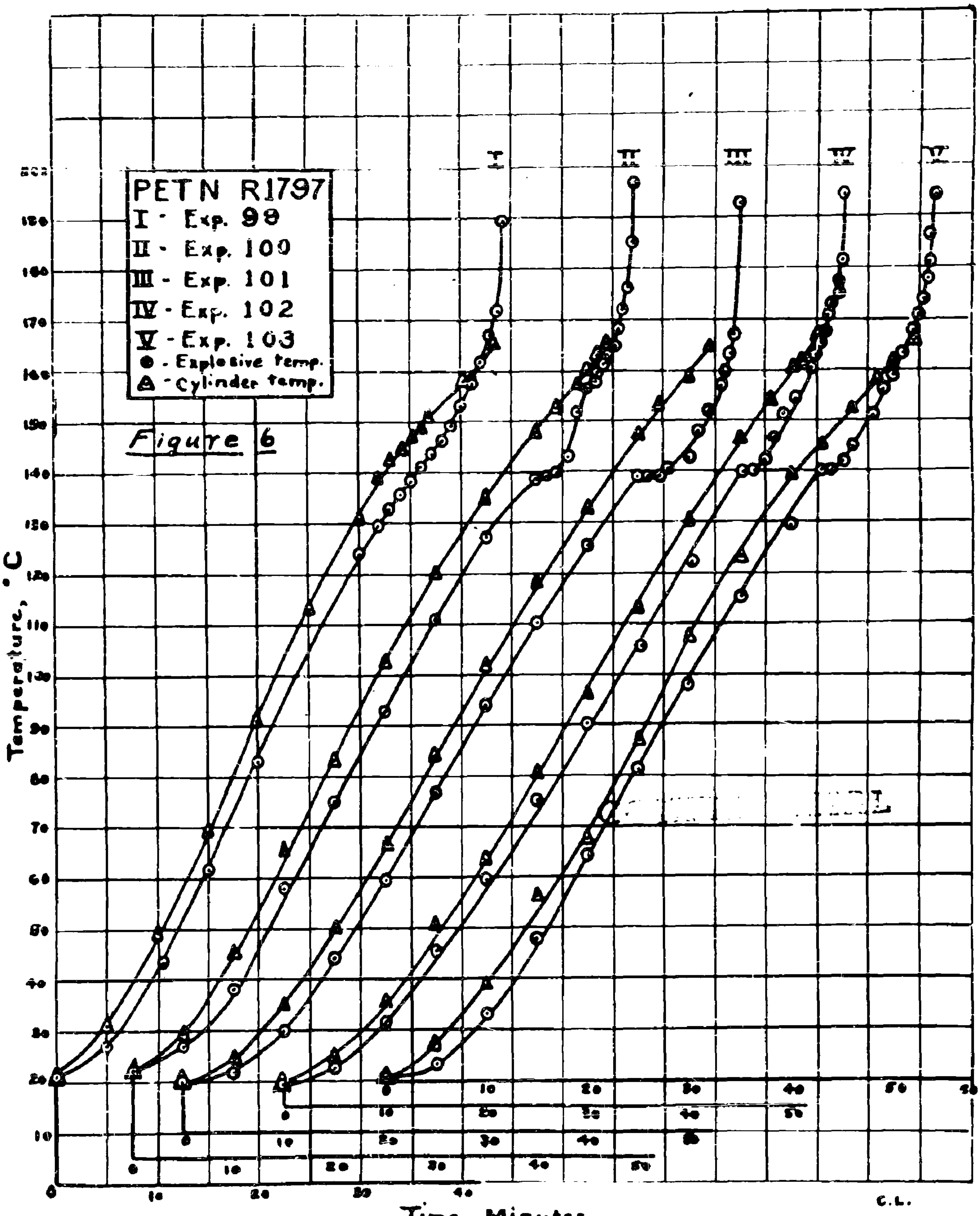
EDNA R1704
I - Exp. 74
II - Exp. 76
III - Exp. 91
IV - Exp. 92
V - Exp. 93
- Explosive temp.
- Cylinder temp.
Temperature, °C
Time, Minutes
I
II
III
IV
V
C.L.

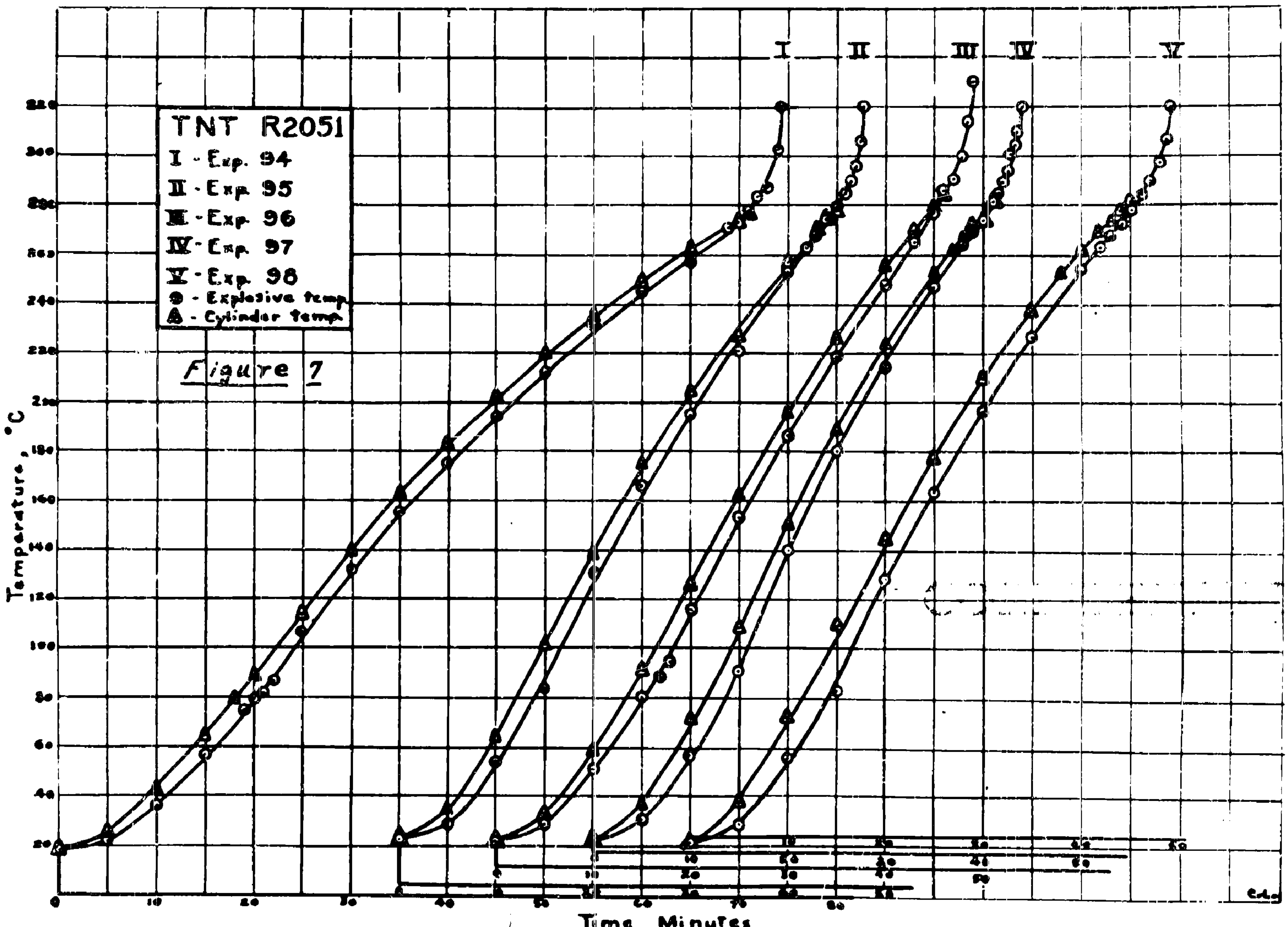
Figure 3


I
II
III
IV
V
Temperature, °C
Time, Minutes
RDX R1975
I - Exp. 77
II - Exp. 88
III - Exp. 89
IV - Exp. 90
V - Exp. 87
⊙ - Explosive temp.
Δ - Cylinder temp.
C.L.
Figure 4



RDX R2106
I - Exp. 104
II - Exp. 106
III - Exp. 107
IV - Exp. 108
V - Exp. 109
⊙ - Explosive temp.
Δ - Cylinder temp.
Figure 5
Temperature, °C
Time, Minutes
C.L.


PETN R1797
I - Exp. 99
II - Exp. 100
III - Exp. 101
IV - Exp. 102
V - Exp. 103
● - Explosive temp.
△ - Cylinder temp.
Figure 6
I
II
III
IV
V
Temperature, °C
Time, Minutes
C.L.



TNT R2051
I - Exp. 94
II - Exp. 95
III - Exp. 96
IV - Exp. 97
V - Exp. 98
- Explosive temp.
- Cylinder temp.
I
II
III
IV
V
Temperature, °C
Time, Minutes

Figure 7

Table I

(1) Experiment Number	(2) Rate of Heating above 100°C. (deg./min.)	(3) Melting Point Range in Heating Curve (°C.)	(4) Time of Explosion (min.)	(5) Bomb Temperature of Explosion (°C.)	(6) Final Recorded Value of Charge Temperature (°C.)	(7) Lower Limit of Explosion Temperature (°C.)	(8) Upper Limit of Explosion Temperature (°C.)	(9) Action of Explosion or Ignition of Charge of Bomb	(10) Melting Point (°C.)
					Tetryl				
77	3.2	129-132	53	174	194	137	177	Split out one side	
78	"	130-136	55	175	195	138	172	Split in half	
79	"	128-133	53	174	197	135	175	" " "	127.5 - 129.9
80	"	128-130	52	176	196	130	175	Split out one side	
81	2.1	123-130	65	171	198	131	173	" " " "	
					Ammonium Picrate				
82	4.9*	--	55	293	306	225	275	Plug blown out; no damage to bomb	
83	5.5	--	44	288	295	225	271	"	
84	4.0	--	57	284	304	232	267	"	265, d.
85	4.3	--	55	237	299	230	270	"	
86	8.3	--	43	291	305	227	273	"	
					Haleite				
74	6.2	--	29	-	174	-	-	Split in half.	
76	2.7	--	58	-	174	-	-	Split out one side	
91	2.8	--	50	176	175	160	173	Split in 3 pieces	178.5 - 179.5, d.
92	2.1	--	62	176	177	162	170	Split in quarters	
93	2.7	--	63	177	176	162	169	Split in 3 pieces	

Table 1 (cont'd.)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
					Bachmann RDX				
75	3.3	190-193	52	206	212	-	192	Cylinder quartered	
									RDX:
87	3.1	190-192	62	213	210	-	191	Split in 3 pieces	201-202.5
88	3.6	186-189	57	213	215	-	189	Cylinder fractured	
									HMX:
89	4.0	186-191	50	209	207	-	192	Cylinder quartered	273-274
90	4.0	---	50	212	213	-	188	Cylinder quartered	(OSRD #652)
					Woolwich RDX				
104	4.0	200-202	47	214	230	188	202	Split in 3 pieces	
106	3.6	199-201	56	211	220	192	202	Split in quarters	
107	3.9	200-203	52	212	206	187	202	" " "	
108	4.1	200-203	55	212	235	178	203	Split in 3 pieces	
109	4.1	---	46	213	220	-	204	Split in quarters	
						PETN			
99	3.2	---	44	167	195			Quartered & bottom out	
100	2.8	138-141	50	172	197			Split in half	
101	2.8	138-140	55	172	193	~140		Split in half	138.5-140
102	3.0	139-141	55	172	195			Quartered & bottom out	
103	2.7	139-140	54	170	195			Split in 3 pieces	
						TNT			
94	3.0*	82-84	75	285	320	220	272	Plug blown out. No damage to cylinder	
95	4.8	--	48	289	320	210	276	"	80-80.5
96	5.5	80-84	49	297	314	225	276	"	
97	5.3	--	44	295	320	-	279	"	
98	4.7	--	49	297	320	-	280	"	

* For Ammonium Picrate and TNT the heating rate is the rate above 200°C.

All charges were 10 grams in weight, pressed to a density of 1.5.

HIGH EXPLOSIVES SENSITIVENESS INVESTIGATION

Report Submitted by
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Sensitiveness to Friction

Recent work with the friction pendulum disclosed that the extrapolated height of fall to produce 50% shots for layers of Cyclonite through 325 mesh having zero thickness is independent of pendulum weight and striker size and shape. These results were obtained with anvils and strikers made of hardened tool steel. The average depth of the minute depressions in the surface, or the roughness, was usually 11 microns. However, in one case the roughness was made 30 microns and the extrapolated height of fall at zero thickness remained the same.

Further determinations of the extrapolated height of fall at zero thickness on hardened steel surfaces having a roughness of 30 microns have been made during the past month.

At the same time the effect of pendulum weight on the height of fall for thick layers has been studied. For this the range of weights has been extended to 20 or 25 kg.

Effect of Layer Thickness

The variation of height of fall with the thickness of layers of Cyclonite has been measured. The Cyclonite was the fraction screening through 325 mesh and the hardened steel anvils and 2 in. x 1/8 in. wheels had a roughness of 30 microns. The weights added to the pendulum were 6, 10 and 20 kg. and the angle of incidence was 4 deg. The results are listed in Table 1 and shown graphically in Figure 1. The dotted curve in Figure 1 is taken from Figure 1 of the preceding report (PT-18, following page 27).

It is evident from the graph that the extrapolated height of fall at zero thickness is no longer equal to 4 cm. for different weights as has been the case until now. It is 4 cm. for 4 kg. but becomes progressively less as the weight increases. Even at thick layers the height is less than 4 cm. for 10 kg. and 20 kg. added weight. For the very heavy weights there seems to be little or no change in height of fall with layer thickness.

Measurements with less weight might show whether or not there is any range of weight in which the extrapolated height at zero thickness is 4 cm. of these surfaces.

Effect of Pendulum Weight

New weights were constructed so that the weight added to the pendulum could be made as much as 20 or 25 kg. Measurements of the height of fall for several weights were carried out on Cyclonite through 325 mesh using 2 in. x 1/8 in. wheels and 1 in. balls as strikers and hardened steel surfaces roughened to 11, 25 and 30 microns. The amount of explosive was about 20 mg./cm.^{2} and the angle of incidence 4 deg.

The results are given in Table 2. It was found that when the heights of fall were plotted against the reciprocal of the pendulum weight as in Figure 2, the curves seemed to be linear although the slope changed at some point along each curve. In some cases this break occurred near the high-weight end of the curve, in others, the low-weight end. However, for all five curves the region of low pendulum weight could be extrapolated to a height of fall of 4 cm. at infinite weight. In the case of the 2 in. x 1/8 in. wheels with roughness of 11 and 25 microns and the 1 in. balls with a roughness of 11 microns the linear portion which was extrapolated was quite long and the extrapolation was fairly definite. In the case of the 2 in. x 1/8 in. wheels with a roughness of 30 microns and the 1 in. balls with a roughness of 25 microns, the linear portion in the low-weight region of the curve was not very long and one cannot say definitely that it was linear. However, the points in this region do lie on or near a straight line through them from a height of 4 cm. at infinite weight.

It will be recalled that 4 cm. was the value obtained previously for the extrapolated height of fall at zero thickness for various strikers and weights when the roughness was 11 microns and for a weight of 4 kg. when the roughness was 30 microns. The striker size and the magnitude of the weight and roughness in those tests were in the range of values at the low-weight end of the curves in Figure 2. It is noteworthy that the roughness values and weights of the curves in Figure 1 which do not extrapolate to 4 cm. at zero thickness produced results which in Figure 2 lie in the high-weight region of the curve and which do not extrapolate to 4 cm. at infinite weight.

Whether or not it is significant that for certain roughness and weight values the extrapolated height of fall at zero thickness is the same as the extrapolated height of fall at zero thickness is the same as the extrapolated height of fall for thick layers at infinite weight, further work may tell.

So much for the extrapolation of the low-weight parts of the curves in Figure 2. The direction of the curves in the region of large weights is not, in general, the same as in the low-weight region. Thus extrapolation of the curves in the region of heavy weights to infinite weight does not lead to a height of 4 cm. In fact, for the 2 in. x 1/8 in. wheels with a roughness of 30 microns and the 1 in. balls with a roughness of 25 microns the curves definitely seem to extrapolate to a height of zero at infinite weight. For the other curves the indications are not so definite but their curvature and direction at the end of the measured region suggest that they also may extrapolate to zero height.

As far as the results go, they seem to indicate that the break in the slope of the curves occurs at progressively smaller weights as the surfaces are made rougher and the areas of contact smaller.

These results show that with very large weights initiation of explosion in thick layers of Cyclonite by frictional impact can take place with very little sliding motion. If the effect of the weight is through the increase in contact time which it causes, as pointed out in the preceding report, these results mean that the longer the duration of the frictional impact the less the relative velocity required to produce initiation.

If this interpretation can be applied to cases of pure friction and other explosives, it helps to make more understandable some of the shots obtained from explosives in bolt threads, valves, etc. In those cases, the duration of the motion may be very long compared with impact times so initiation might occur with relatively low shearing velocities.

Future Work

More data would be desirable to elucidate the relation, if any, between the extrapolated height at zero thickness and the linearly extrapolated height at infinite weight.

The effect of weight and layer thickness for other particle sizes and explosives will be studied.

Experimental

In these experiments the apparatus used was the Hercules Friction Pendulum described in a Special Formal Progress Report on this investigation: "A Method of Measuring the Sensitiveness of High Explosives to Frictional Impact", OSRD No.3185.

The layers of explosive were made with the set of gages described in PT-17, page 16. The Cyclonite used was obtained from Bruceton and was made by the Woolwich method.

The new heavier weights were made of steel, weighed 5 kg., and measured 7-1/2 in. in diameter and 15/16 in. thick. They had a hole in the center and a slot for slipping them onto the pendulum the same as the weights with the original Bureau of Mines pendulum. Four of these weights were made up.

The surfaces with a roughness of 30 microns were made by sand-blasting with No.10 corundum abrasive. The depth of the markings on the surface were not very much greater than those on the surfaces having a roughness of 25 microns as indicated by the figures 30 and 25. This, however, is not a complete description of the difference between these two surfaces. The horizontal distances between the peaks or depressions were about 5 or 10 times greater on the 30 than on the 25 micron surfaces. This apparently is responsible for the fairly large differences in heights of fall that were observed. This illustrates the difficulty in giving a quantitative measure of roughness which describes all the features of the surface important in initiation.

Because of the statistical fluctuation in the results and the error in the thickness for the thin layers, the figures in Tables 1 and 2 are the means of several determinations, in some cases 5 or 6. For the low heights of fall, especially, the individual results seemed to scatter, the range being as much as 100%.

TABLE 1

Effect of Layer Thickness on Sensitivity to Frictional Impact of Cyclonite Through 325 Mesh

Anvils - hardened Stentor steel
Wheels - hardened Stentor steel, 2 in. diameter, 1/8 in. thick
Surfaces - sand-blasted with No. 10 corundum, roughness 30 microns
Angle of Incidence - 4 degrees

Gage Thickness in Inches	Layer Thickness in mg./cm.^{2}	Height of Fall for 50% Shots - in cm. 6 kg.	10 kg.	20 kg.
0.0008	1.3	4.2	3.1	1.5
0.0020	1.7	3.8	2.4	1.9
0.0026	1.9	3.9	3.3	1.3
0.0039	2.3	3.4	2.5	1.6
0.0063	3.3	3.7	2.3	1.5
0.0079	4.7	4.5	2.5	1.6
0.012	10.9	4.9	3.4	1.3
0.016	17.3	5.6	4.0	1.7

TABLE 2

Effect of Pendulum Weight on Sensitivity to Frictional Impact of Cyclonite through 325 Mesh

Anvils, wheels and balls - hardened Stentor steel
Angle of Incidence - 4 degrees
Amount - about 20 mg./cm²

Added Weight	Total Pendulum Weight = M	1/M	Height of Fall for 50% Shots (cm.) 2 in. x 1/8 in. wheels 30μ	25μ *	11μ	1 in. Balls 25μ	11μ *
2 kg.	3.7 kg.	0.27 kg.$^{-1}$	13	19	32**	11.0	18
3	4.7	0.21	11.0	16	24	10.4	14
4	5.7	0.175	10.7	13	20	9.1	13
6	7.7	0.130	7.3	11	15	7.7	11
10	11.7	0.085	4.9	8.5	12	5.3	8.4
15	16.7	0.060		4.8	9.7		5.9
20	21.7	0.046	2.3	4.6	7.8	2.5	4.9
25	26.7	0.038		2.5	6.0		4.7

*Only one curve was drawn through these two sets of points in Figure 2 to avoid the confusion of too many lines in the graph. The error introduced by this is not large and does not affect the linearly extrapolated heights at infinite weight.

**This value was more or less ignored in drawing the curve. It seems to be high when comparison is made with 27 cm., the result of the same measurement given in Figure 2 following page 16 of PT-17.

VARIATION OF HEIGHT OF FALL WITH LAYER THICKNESS FOR CYCLONITE THROUGH 325 MESH

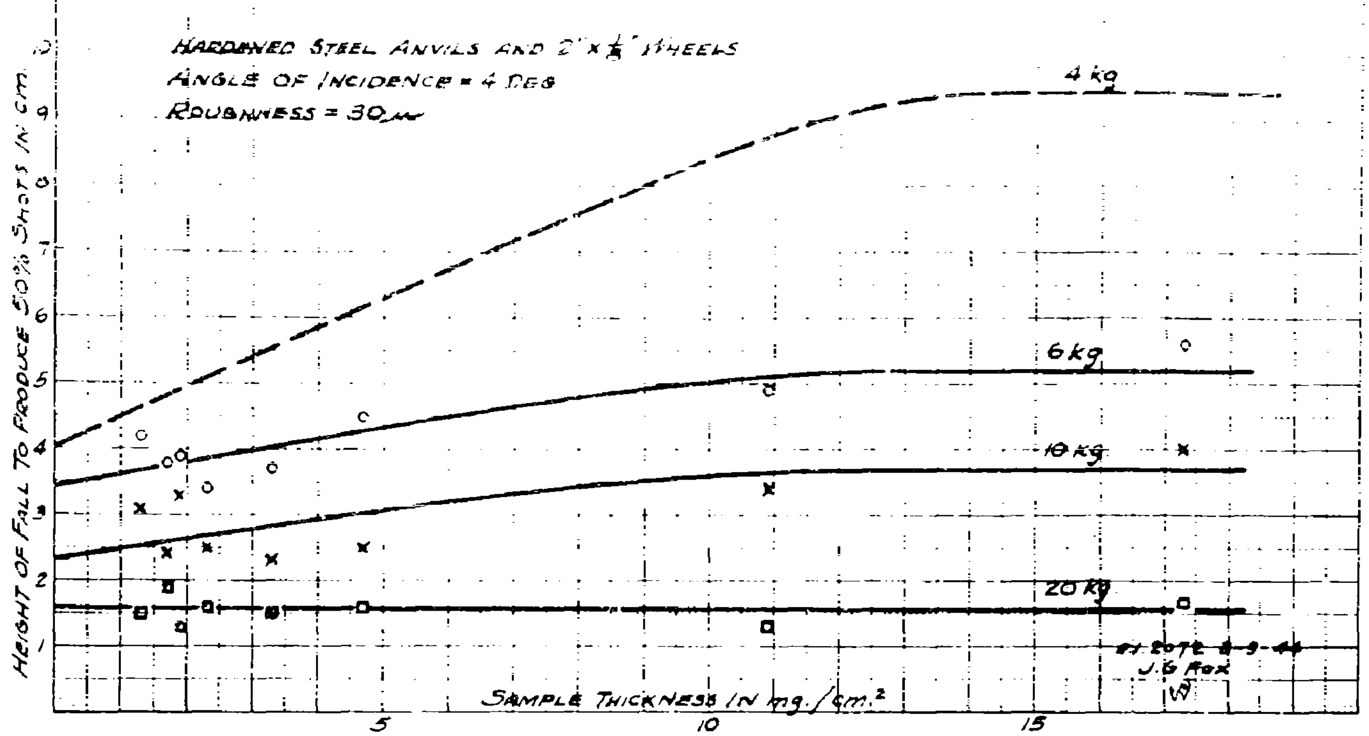
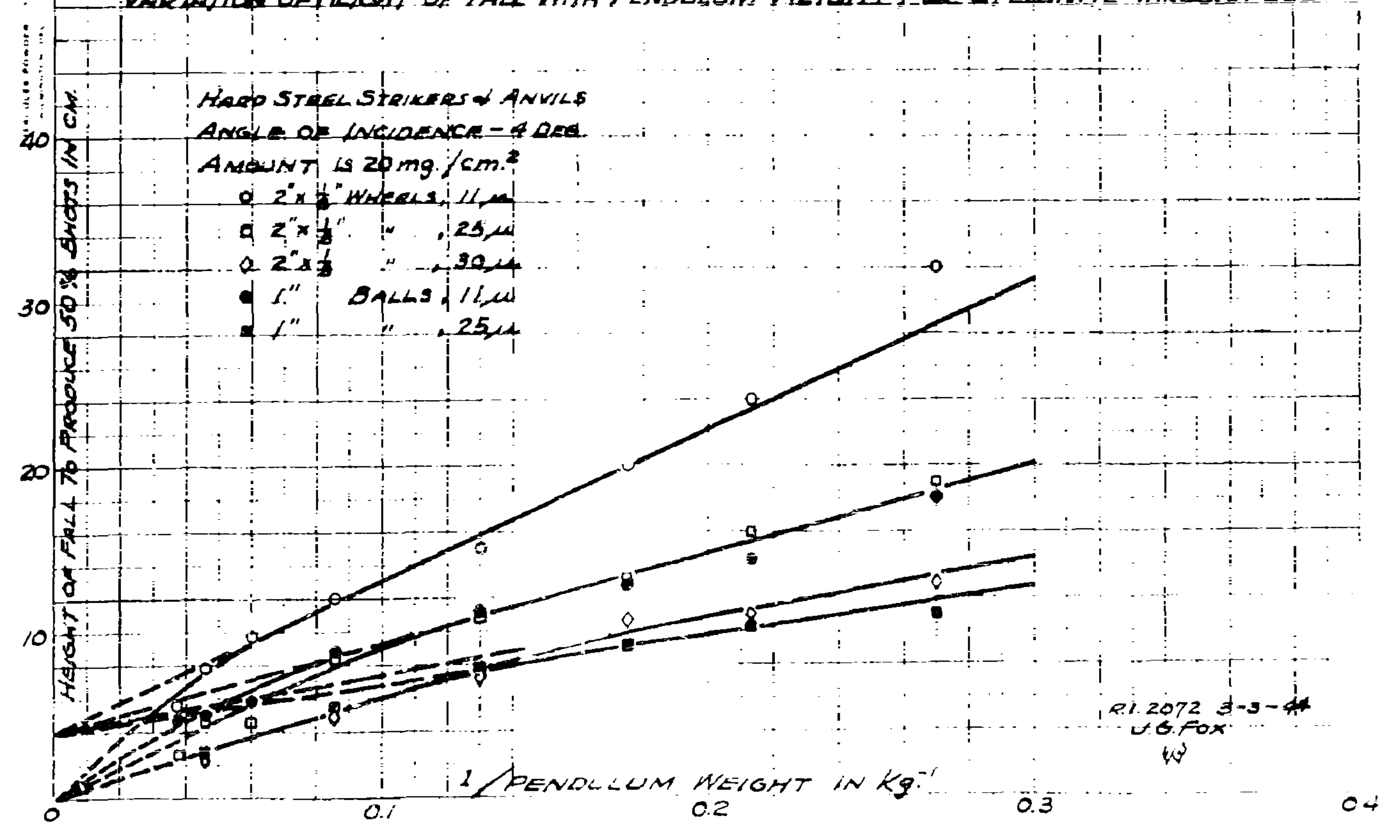


FIGURE 2

VARIATION OF HEIGHT OF FALL WITH PENDULUM WEIGHT FOR CYCLONITE THROUGH 325



STUDIES OF THE PREPARATION, STABILIZATION AND TESTING OF EXPLOSIVES

Report Submitted by
F. H. Westheimer
Explosives Research Laboratory
Bruceton, Pa.

The Theory of Thermal Stability Tests

(H. Henkin)

Introduction and Summary

The Hercules Powder Co.[1] has recently introduced an adiabatic ignition test for smokeless powders. They point out that this new test is better than the 135°C. ignition test because under adiabatic conditions the time it takes for a sample of powder to ignite should be, and within the limits tested actually is, independent of the size of the sample. A further advantage of the test, and an advantage which has not heretofore been pointed out, is that this test, in contrast to other thermal stability tests, is capable of a simple theoretical treatment.

In a recent report, Parlin, Duffy, Powell & Eyring[2], have derived the equations for the time-temperatures relationship in a purely thermal explosion. The assumptions made in the derivation of Eyring's equation are these: the explosive is heated by the decomposition of part of the sample, and the rate of the decomposition increases (with a corresponding increase in the rate at which heat is produced) with increasing temperature. Since the explosion takes place in an extremely short space of time, it must necessarily be adiabatic. The equations derived by Eyring can, with certain modifications, be applied to the adiabatic thermal stability test, provided that the rate of decomposition increases from purely thermal causes (i.e., provided there is no autocatalysis). Of course, the equation would apply strictly only to the case where a non-stabilized explosive containing only one reactive group decomposes thermally to the final reaction products. The equation must necessarily be modified to meet the actual, more complicated conditions.

A crude apparatus for adiabatic thermal stability testing has been constructed at Bruceton, and a few orientation experiments carried out with NENO, N,N' dinitrodi- (β-nitroxyethyl) oxamide. This is one of a group of explosives for which the rate and activation energy of decomposition are known[3]. A comparison of the adiabatic heating experiments with Eyring's equation is probably somewhat premature, owing to the fact that the experiments are, at the present time, very crude. The agreement between theory and experiment seems, however, fully to justify the hope that a complete theory for the adiabatic test will shortly be available.

Experimental

Apparatus

The present crude apparatus for adiabatic measurements consists of a thermostat, constructed of a large aluminum block. Holes have been bored in the block, and in one of these holes a tube containing the explosive is suspended. One junction of a copper-constantan thermocouple is immersed in the explosive, while the other junction of the thermocouple is placed in another well in the aluminum block. The thermocouples are connected to a Fisher type 11-506-27L galvanometer. The temperature of the thermostat can be controlled manually, and it was so adjusted that the galvanometer reading was always zero. In this way the temperature difference between the explosive and the thermostat was kept at less than 0.05°C. The "coefficient of thermal leakiness"[4] between the explosive and the block, however, is unduly high, and the apparatus as it stands is far from satisfactory.

Theory

The following is a slight modification of Eyring's theory.[2]

Let $\underline{x}$ be the concentration of primary reaction product, in m/l
Let $\underline{a}$ be the initial concentration of explosive in m/l
Then

$$dx/dt = Z(a-x)e^{-A/T} \qquad (1)$$

where $\underline{Z}$ is the "collision factor", $\underline{A}$ is $\Delta H^*/R$ (ΔH^* is the heat of activation), $\underline{T}$ is the absolute temperature and $\underline{t}$ is the time. Since the thermal stability test is concerned only with the first few percent of reaction, the equation is well approximated by

$$dx/dt = Zae^{-A/T} \qquad (2)$$

The temperature of the reaction at any time, $\underline{t}$, is given by the equation

$$T = T_o + \frac{x\,Q_p}{a\,C} \qquad (3)$$

where T_o is the initial temperature of the explosive, C is the specific heat of the material in calories/mol and Q_p is the "partial" heat of reaction in calories/mol. This quantity is not the same as the heat of explosion, but is rather that heat which is generated by whatever incomplete decomposition reaction occurs at low temperatures. Equation (3) can be transformed into (4) -

$$\frac{dT}{dt} = T_p Z e^{-A/T} \qquad (4)$$

where $T_p = \frac{Q_p}{C}$. Upon integration (4) yields (5)

$$t = \frac{1}{ZT_p} \left[Te^{A/T} - T_o e^{A/T_o} + AE_i\left(\frac{A}{T_o}\right) - AE_i\left(\frac{A}{T}\right) \right] \qquad (5)$$

where E_i (x) is the exponential integral, $\int_{-\infty}^{x} \frac{e^x}{x} dx$.

As a good first approximation[2] this reduces to

$$t = \frac{1}{AZT_p} \left[T_o^2 e^{A/T_o} - T^2 e^{A/T} \right] \qquad (6)$$

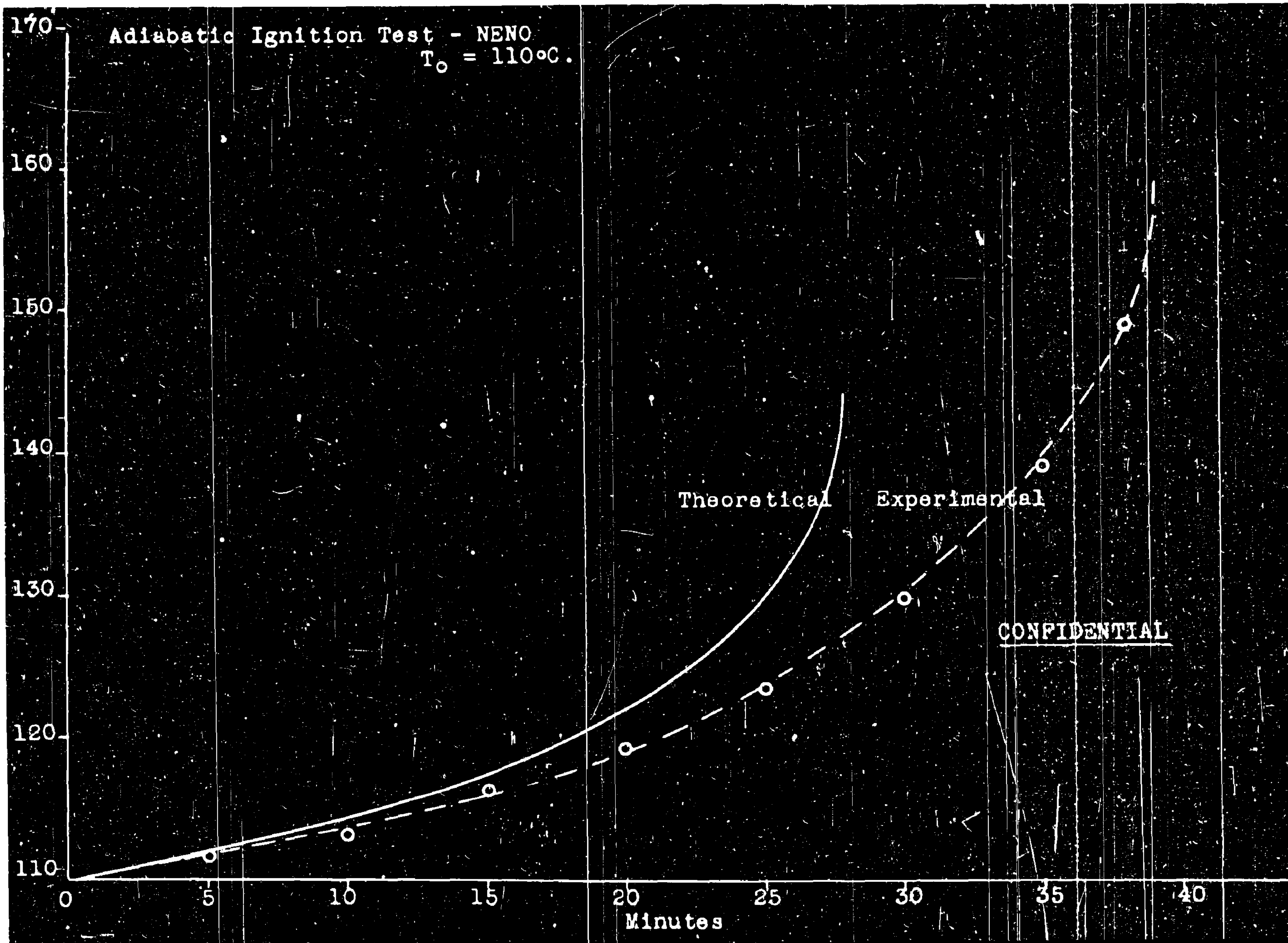
This is the fundamental equation relating time and temperature in the adiabatic thermal ignition test.

Experiments with NENO

A few experiments have been carried out with NENO at 110° and 120°C. The available data have been summarized in Table 1 and a particular experiment has been plotted in Figure 1. Although the data are only approximate, the graph does illistrate the fact that the theory faithfully reproduces the shape of the experimental temperature-time curve.

Table 1

Temperature	Time of Ignition (in minutes)	
	Calc.	Found
110°	28	36, 38
120°	13	20, 20


Adiabatic Ignition Test - NENO
T_o = 110°C.
Theoretical
Experimental
CONFIDENTIAL
170
160
150
140
130
120
110
0
5
10
15
20
25
30
35
40
Minutes

The data needed for the calculation in Table 1 and Figure 1 were obtained as follows: The rate of decomposition of NENO has been measured[3], for the liquid (or solution in TNT) at several temperatures in the range from 75° to 120°C. The energy of activation is about 35,000 calories, and the decomposition has been found to yield about three moles of gas for each mole of NENO (as compared with 13 moles of gas, including steam, from the complete explosion). The reaction has a rate constant of 4×10^{-6} sec.$^{-1}$, at 100°C. Equation (6) involves the activation energy for the decomposition of NENO, and the "collision factor" which can be calculated from the activation energy and the rate constant. The only unknown in equation (6) is T_p. This constant can, however, be calculated from the initial temperature rise in the adiabatic stability test, since

$$T_p = Q_p/C = m/k \qquad (7)$$

where m is the initial temperature rise per second at any temperature and k is the rate constant, in inverse seconds, for the decomposition at this same temperature. At 110°C., m is about 0.0040 sec.$^{-1}$, and T_p is therefore of the order of 1000°C. The calculated temperature of explosion, T, of NENO is 3900°C. (using a value of 0.32 cal/g, calculated from Kopp's rule, for the specific heat and 1260 cal/g for the heat of explosion). The value of T_p is then about 25 percent of the value of T , and Q_p, the heat of the decomposition reaction, is about 25% of the heat of explosion. These figures seem entirely reasonable; since the chemical reactions involved in the low temperature decomposition of NENO are at present unknown, a definite confirmation of the heat of the partial reaction cannot be obtained.

Since the values of A, Z and T_p have been obtained experimentally, there are no arbitrary parameters in equation (6). However, T_p is determined from the same data which is later compared to equation (6), and it is therefore possible to regard this quantity as a parameter. If this point of view is adopted, it is then necessary to point out that the value of T_p (about 25% of T) is a highly reasonable one. It should further be pointed out that equation (6) is independent of the number of moles, n, of gas generated per mole of NENO in the low temperature decomposition of the compound. The value of n appears in both Z and in T_p, but cancels out of the product AZT_p, which occurs in equation (6). More precise work in this field is now in progress.

Aluminized Explosives

(S. D. Brewer, J. W. Dawson)

A program has been set up to study alumized explosives. The work can be divided roughly into two parts (A) theoretical and (B) practical.

(A). It has been postulated that aluminum acts in the presence of ammonium nitrate to reduce the nitro groups of the TNT in Minol, much as zinc reduces nitrobenzene to phenylhydroxylamine in the presence of ammonium chloride. Further, it seems altogether possible that aluminum reduces the nitro groups of the RDX either in Torpex, or in DBX, or in both. This reducing action of the aluminum on the organic matter would be superimposed upon the reaction of the aluminum with ammonium nitrate to generate ammonia. The aluminum used analyzes 97.3 percent aluminum, the rest presumably being a mixture of aluminum oxide and other metals. After a sample of wet Minol has been heated for 24 hours, the residual aluminum-aluminum oxide mix contained only 81.8 percent aluminum. Further, during the reaction colored products have been produced from the TNT. These products are now under investigation.

(B). It has been postulated that the reactions between aluminum and TNT, ammonium nitrate and RDX can be eliminated by coating the aluminum with a thin layer of inert material. It has proved possible to coat the aluminum with a thin layer of aluminum phosphate or with some aluminum lakes. Work similar to that in progress at Bruceton has also been reported from other laboratories[6,7]. These lakes are prepared by treating finely divided aluminum with acqueous solutions of appropriate dyestuffs. Those dyes were used which are known to produce insoluble precipitates with aluminum hydroxide. A pale purple aluminum powder has been prepared using either alizarin or aurin tricarboxylic acid. Insufficient tests are at present available to show whether these samples of coated aluminum are more or less resistant to attach by ammonium nitrate, TNT and RDX than the uncoated material. A detailed account of this work will be made in the next report.

Preparations and Testing

(A. Turk)

Purification of Cyclopentanone.

In a previous report[8] it has been shown that some samples of cyclopentanone are unsuitable for the synthesis of Fivone. A simple and adequate procedure for the purification of duPont cyclopentanone, sample A-3443, follows.

Crude cyclopentanone (420 grams) was mixed with syrupy phosphoric acid (62 grams) and refluxed gently for ten minutes. The mixture was then cooled to 50°C. and distilled under partial vacuum at 50-80°C. The distillate (398 grams) of wet cyclopentanone was quite suitable for Fivone synthesis.

Preparation of Sixone.

A series of preparations of Sixone from cyclohexanone and formaldehyde has been carried out, using magnesium salts rather than calcium salts as catalysts. The product consisted of a mixture of Sixone and Sixol, similar to that obtained when calcium hydroxide is used as catalyst; the yield in the most favorable case, however, is greater than that obtained previously with calcium hydroxide as catalyst. In general, it can be said that magnesium hydroxide, magnesium carbonate and basic magnesium carbonate are less effective than magnesium oxide. The best procedure so far found is given below.

Purified cyclohexanone (50 grams), water (200 cc.), 37 percent formalin (155 cc.), and magnesium oxide (5 grams) were stirred together, and then allowed to stand at room temperature with occasional shaking for 22 days. At the end of the reaction time the mixture was filtered, neutralized with dilute hydrochloric acid, and evaporated to dryness. The oily residue was taken up in 50 cc. of acetone and the solution allowed to stand at room temperature. The crystals which separated were crude Sixone, 93% of theoretical, m.p. 108-114°C. (m.p. of pure Sixone, 143°C.)

Nitroglycerine

A total of 90 pounds of nitroglycerine was prepared at Bruceton for laboratory use.

Stability Tests

A total of 273 chemical stability tests was carried out. This included 137 thermal stability tests, 30 vacuum stability tests, 44 Bergmann-Junk determinations, and 62 miscellaneous tests.

References

(1) Koski, RD 4 (Hercules Report) Dec. 20, 1943

(2) Parlin, Duffy, Powell and Eyring, OSRD Report No. 2026, November 13, 1943.

(3) H. Henkin, unpublished work

(4) White, Modern Calorimetry, Chemical Catalogue Co.

(5) OSRD Report No. 702

(6) WA-1628-14

(7) A communication from the Naval Ordnance Laboratory indicates that they have also succeeded in coating aluminum with various lakes.

(8) OSRD Report No. 1767

DEVELOPMENT OF LIQUID EXPLOSIVES

Report Submitted by
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Liquid Explosives Based on DNT-TNT-Tetryl-P.A.

The results of investigations reported in Division 8 Interim Report PT-18 under this heading indicated that a non-NG liquid explosive suitable for Mark 8 could not be developed with the ingredients considered (DNT, TNT, Picric Acid, Tetryl, and PETN). It was believed, however, that mixtures of DNT, TNT, and Tetryl sensitized with NG might have a number of worthwhile advantages over the NG-dimethyl phthalate mixtures developed at the ERL.

Preliminary Tests with DNT-TNT-NG (Glycol Oil Mixtures)

In preliminary tests it was found that Tetryl was soluble only to the extent of about 1 to 2% in DNT-TNT mixtures containing 25 to 50% NG. Consequently, two series of compositions, the first comprising NG and DNT oil and the second NG, DNT and TNT (DNT/TNT ratio = 7/3), were shot in 1-1/2 x 9 in. cans with U. S. Engineers (13.5-gr. PETN) caps to determine the minimum percentage of NG required for complete detonation. It was found that 60% NG was required for the DNT oil series and 45% for the DNT-TNT series. To save time a 30% glycol-NG oil was used in these tests even though it was known that a polymer oil would be more desirable because of its lower vapor pressure.

On the basis of these results compositions containing (a) 50% NG, 35% DNT oil and 15% TNT, and (b) 60% NG and 40% DNT were selected for further study. The results of these tests are given in Table 1. Although both mixtures had good explosive properties, the melting point of the DNT oil mixture (above -6°C) was too high.

DNT-TNT-NG Compositions Made with Polymer Oil

As the preliminary results indicated that DNT-TNT-NG mixtures might be very satisfactory for Mark 8, the orientation experiments were repeated using the more desirable No. 3 NG (31% polymer).

In order to determine the range of compositions suitable for Mark 8, the minimum percentage of NG was determined by underwater propagation tests, using 2-in. diameter hose, and the upper limit of NG was investigated by means of cap sensitiveness tests. It was found that 50% NG (35 DNT and 15 TNT) was required for propagation in 2-in. diameter (8-10 ft. lengths) under water. On the other hand, the cap sensitiveness studies showed that a 60% NG composition (28 DNT and 12 TNT) was somewhat less sensitive than the ERL 80-20 and 75-25 NG-DMP mixtures. This NG composition gave consistent detonations with a U. S. Engineers cap (13.5-gr. PETN) and consistent failures with a No. 6 Tetryl cap. The 80-20 NG-DMP mixture detonated once in three trials with a No. 3 fulminate cap and the 75-25 mixture gave one detonation out of ten trials with a No. 5 cap (PT-18). While it was not considered necessary to use more than 60% NG, a few tests were made with 75% NG composition; one detonation and three failures were obtained with a No. 1 cap. These results indicated that the cap sensitiveness of the ERL 80-20 NG-DMP mixture probably would be duplicated by a DNT-TNT-NG mixture containing 65-70% NG.

Viscosity tests on a 55% NG mixture (31.5 DNT and 13.5 TNT) at 0° and 20°C gave values of 211 and 45 centipoises, respectively, as compared with 250 and 50 centipoises reported by ERL for their 80-20 NG-DMP mixture.

Mixtures containing 50 and 55% NG were tested at Millville (in air) for propagation and velocity in 2-in. and 4-in. diameter hose. The 50% NG mixture propagated at high velocity (6950 m./sec.) in 4-in. diameter (5-ft. length) and through about half of the 25-ft. length in 2-in. diameter, the second half of the 2-in. diameter charge propagating at low velocity. The 55% composition propagated through 25 ft. of the 2-in. hose and 5 ft. of the 4-in. hose at 7170 m./sec. and 7090 m./sec., respectively.

No detonations were obtained in bullet tests with either the 55% or 60% NG mixture in open 4 x 4-in. cans backed by wood. With steel backing, however, the 60% NG mixture gave one detonation out of three trials and the 55% mixture gave two ignitions and one weak partial detonation out of ten trials.

Details of all of the tests on 50, 55 and 60% NG mixtures are given in Table II in comparison with similar data for the ERL NG-DMP mixture. On the basis of these results it is believed that the 55% NG (31.5 DNT and 13.5 TNT) composition should be entirely satisfactory for Mark 8. Its low impact, friction (sliding rod test), bullet and cap sensitivity as well as its low viscosity appear particularly desirable. On the other hand, if a more powerful mixture were desired, 60% NG and probably 65% could be used without making the mixture too sensitive.

Calculated Energies and Explosion Pressures

The methods described in the Eastern Laboratory report "Theory of Detonation" were used to calculate the maximum available energy, the theoretical velocity and the detonation and explosion pressures of the ERL 80-20 and 75-25 NG-DMP mixtures, and the Eastern Laboratory 60-28-12 and 55-31.5-13.5 NG-DNT-TNT mixtures. The results of these calculations for a density of 1.5 are summarized in Table III.

Assuming that all of these compositions would have the same density, the detonation pressure of the EL 55% NG composition would be the same as that of the ERL 80-20 NG-DMP mixture. However, its maximum explosion pressure and available energy would be about 3% and 8% lower, respectively, than for the ERL composition. On the other hand, the EL 60% NG formula would have about the same energy and 4-5% higher detonation and explosion pressures than the ERL 80-20 explosive. Any of these compositions should be definitely superior to TNT. For example, the available energy and detonation pressure of the 55% NG mixture would be 22% and 52% higher, respectively, than for TNT at a density of 1.4.

Future Program

Although no further experimental work is planned on NG-DNT-TNT liquid explosive mixtures, the 150°F storage tests will be continued.

It is expected that the Laboratory will be called on to prepare several hundred pounds of the ERL 80-20 NG-DMP mixture for tests by the Navy at Stump Neck. It is hoped that arrangements can be made for tests on the Eastern Laboratory 55-31.5-13.5 or 60-28-12 NG-DNT-TNT mixtures at the same time.

Table I

PROPERTIES OF LIQUID MIXTURES OF NG (GLYCOL OIL), DNT AND TNT

	DNT Oil Series	DNT-TNT(7/3)Series
Per cent NG necessary for detonation with U.S. Eng. Cap in 1-1/2x9" cans	60	45
Selected composition		
NG (#19)	60	50
DNT (oil)	40	35
TNT		15
Centralite 1	0.3	0.25
Density		1.44
Sensitiveness to small arms fire -4x4" open cans (.30 caliber Springfield rifle)		
a. Wood backing	6 F	10 F
b. Steel backing	2 F , 4 I, 0 D	4 F , 2 I, 0 D
Mortar (T.V.)	12.4	12.4
Viscosity at 0°C	55 Centipoises	72 Centipoises
Freezing point	> -6°C	< -6°C
Stability		No gas after 6 days at 150°F with or without pieces of rubber added
Drop Tests (10-lb. weight)		
a. Plain	48" - 0 D, 10 F	48" - 0 D, 10 F
b. Filter paper	48" - 0 D, 10 F	48" - 0 D, 10 F
Sliding Rod (10-lb rod)		
a. Plain	60" - 0 D, 10 F	60" - 0 D, 10 F
b. Filter paper	60" - 0 D, 10 F	60" - 0 D, 10 F

Velocity (4"x5' rubber hose) - 2x8" Cast Pentolite Primer meters/second

Distance from Primer	1	2	1	2
2-1/2' (12" spacers)	7170	6980	6980	7390
3'	6850	6980	6850	6980
4'	6980	7530	7100	7100
4-1/2'	6980	6980	7100	7050
avg.	6945	7120	6980	7130

Table II

Mark 8 Liquid Explosives

	EL Mixtures			ERL Mixtures		
Composition						
NG (#3 polymer oil)	60	55	50	80	75	70
Dimethyl phthalate				20	25	30
DNT Oil	28	31.5	35			
TNT	12	13.5	15			
(Centralite 1 - 1/2% of NG in all cans)						
Density	1.51	1.50	1.50	--	1.45-1.50	1.45-1.47
Sensitiveness to small arms fire - 4x4" cans - .30 cal. Springfield rifle						
a. Wood backing	10F	10F	--			
b. Steel backing	2F,1D	7F, 2I, 1(Weak)PD	--			
Mortar (T.V.)	12.7	12.6	11.5	--	11.1	10.8
Viscosity - 0°C.	221	211				
20°C.	47	45				
Freezing Point °C.	< -10	< -10	< -10			
Stability	-	No gas after 6 days at 150°F. with or without pieces of rubber added.	Same as 55%			
Drop Tests (10-lb. weight)						
a. Plain	48"-10F	48"-10F	--	48"-10F	--	--
b. Filter paper	48"-10F	48"-10F	--	48"-10F	--	--
Sliding Rod (10-lb. rod)						
a. Plain	66"-10F	66"-10F	--	60"-10F	--	--
b. Filter paper	66"-10F	66"-10F				

Table II (Cont.)

	EL Mixtures			ERL Mixtures				
	60-28-12	55-31.5-13.5	50-35-15	80-20	75-25		70-30	
Cap Sensitiveness								
#2				0D, 10F	-		-	
#3				1D, 2F	-		-	
#4				1D, 1F	0D, 10F		-	
#5				-	1D, 9F		-	
#6 Tetryl cap	10F	-	-	-	-		-	
#8 Tetryl cap	3D, 7F	0D, 10F	-	-	-		-	
9.5 gr. PETN Test cap	8D, 2F	9D, 1F	0D, 1F	-	-		0D, 10F	
13.5 gr. PETN U.S.Eng.cap	10D, 0F	10D, 0F	0D, 3F	-	-		2D, 1F	
2-13.5 gr. PETN U.S.Eng.caps	-	-	8D, 0F					
Velocity								
Distance from primer (12" spacers)					1	2	1	2
2" dia. 25' length 5 ft.		7100	6490					
10		7240	6600					
15		7240	<3750					
20		7100	"					
Avg.		7170	-					
4" dia. 5-6' length 2		7310	6970		6050	No record*	7260	No record**
2-1/2		7100	7035		5780	" "	7180	" "
4		7100	6850		7920	" "	8580	F
4-1/2		6850	6970		8120	" "	8720	F
Avg.		7090	6950		6970		7930	

* Propagate through 6-ft. column at low velocity

** Failed to propagate through 6-ft. length

TABLE III

THEORETICAL COMPARISON OF ERL NG-DMP MIXTURES WITH EASTERN LABORATORY NG-DNT-TNT MIXTURES

	ERL Mixtures		EL Mixtures	
Composition				
NG	80	75	60	55
Dimethyl phthalate	20	25		
DNT			28	31.5
TNT			12	13.5
Density (assumed)	1.5	1.5	1.5	1.5
A (kg.cal./kg.) (Max. available energy)	1020	820	1010	935
A/77 (T.V. units)	13.3	10.7	13.2	12.1
$P_3 \times 10^{-3}$ (atm.) (Explosion pressure)	88	73	92	85
$P_2 \times 10^{-3}$ (atm.) (Detonation pressure)	175	160	184	175
Theoretical velocity (m./sec.)	7200	7000	7350	7150

DETERMINATION OF HEATS OF COMBUSTION

Report Submitted by
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University of Pittsburgh

Note: Previous work on this subject has appeared in Division 8 Interim Reports PT-7, pages 34 ff. and PT-10, pages [illegible] ff.

Ethylenediaminedinitrate (EDDN)

Sample No.	Origin of Sample	Date of Work
R-[illegible]175-[illegible]	ERL Bruceton, Pa.	2/15/44

Formula	Mol. Wt.	Density	Cp	M.P.
$C_2H_{10}O_6N_4$	186.13	1.42	0.30	--

Heat of Combustion Data

$-\Delta U_{B/M}$	$-\Delta U_B$	$-\Delta U_R$	$-\Delta H_R$	$-\Delta H_f$
2017.45 2016.15 2015.19	375.29	374.70	373.22	157.29

2016.26 ± .79 = Mean
(± 0.04%)

Remarks

$-\Delta U_{B/M}$ = Heat of combustion in cal./g. for bomb process.

$-\Delta U_B$ = " " " " k. cal./mole " " "

$-\Delta U_R$ = " " " " " " / " at 1 Atm. constant V.

$-\Delta H_R$ = " " " " " " / " " 1 " " P.

$-\Delta H_f$ = " " formation " " " / " " standard conditions.

MeNENA (N-methyl-N-(β nitroxyethyl) nitramine)

Sample No.	Origin of Sample	Date of Work
CU-F-16 R2303	ERL Bruceton, Pa.	2-14-44

Formula	Mol. Wt.	Density	C_p	M.P.
$C_3H_7O_5N_3$	165.11	1.52	0.30	--

Heat of Combustion Data

$-\Delta U_{B/M}$	$-\Delta U_B$	$-\Delta U_R$	$-\Delta H_R$	$-\Delta H_f$
2881.62 2882.96 2880.89	475.82	475.17	473.84	48.68

2881.82 ± 0.76 = Mean
(± 0.03%)

Remarks

$-\Delta U_{B/M}$ = Heat of combustion in cal/g. for bomb process

$-\Delta U_B$ = " " " " k.cal./mole " " "

$-\Delta U_R$ = " " " " " " / " at 1 Atm. constant V.

$-\Delta H_R$ = " " " " " " / " " 1 " " P.

$-\Delta H_f$ = " " formation " " " / " " standard conditions.

Pentryl

Sample No.	Origin of Sample	Date of Work
R-564-C	ERL Bruceton, Pa.	2/10/44

Formula	Mol. Wt.	Density	C_P	M.P.
$C_8H_6O_{11}N_6$	362.18	1.83	0.30	--

Heat of Combustion Data

$-\Delta U_{B/M}$	$-\Delta U_B$	$-\Delta U_R$	$-\Delta H_R$	$-\Delta H_f$
2600.41 2599.34 2602.62	941.95	940.05	935.91	24.84

2600.79 ± 1.22 = Mean
(± 0.05%)

Remarks

$-\Delta U_{B/M}$	=	Heat of combustion in cal./g. for bomb process.
$-\Delta U_B$	=	" " " " k. cal./mole " " "
$-\Delta U_R$	=	" " " " " " / " at 1 Atm. constant V.
$-\Delta H_R$	=	" " " " " " / " " 1 " " P.
$-\Delta H_f$	=	" " formation " " " / " " standard condition:

STUDIES OF THERMAL STABILITY TESTS

Report Submitted by
R. C. Elderfield
Columbia University

Vacuum stability rate studied have been continued on Haleite at several temperatures from which energy of activation data may perhaps be calculated. The rate of gas evolution and analysis of the evolved gas are shown in the tables below and accompanying curves.

Haleite: duPont lot 26 recrystallized (received from Picatinny). Dried one day at 100°C. 0.5 g. sample. Temp. of test: 150°C. Evacuated 0.5 hr. at 120° before starting readings. Figure I and curve b in Figure II.

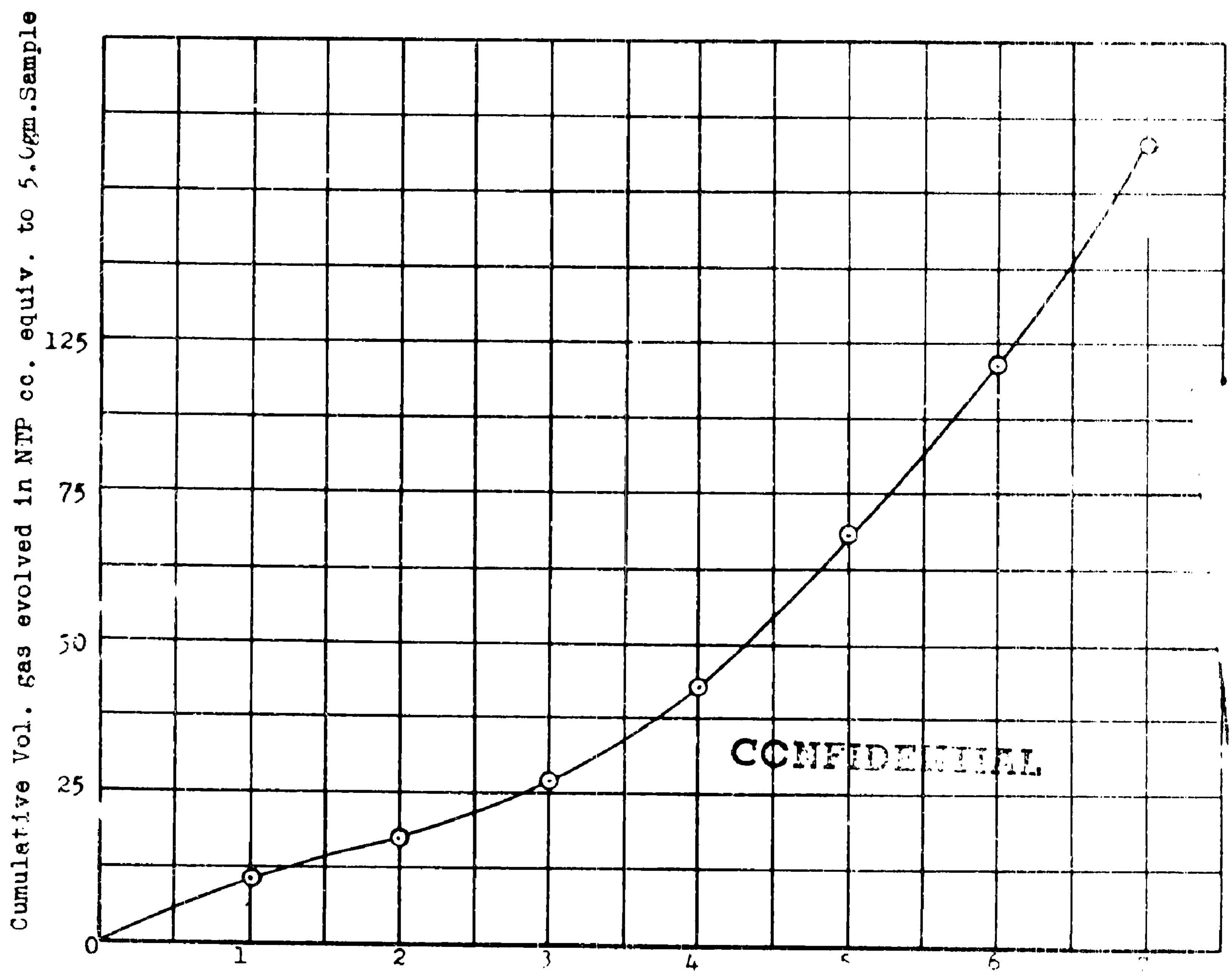
	gas sample taken at		
	5 hrs.	7 hrs.	11 hrs.
Oxygen	0%	0%	0%
Moisture (Note 1)	17.6	7.9	3.9
Basics	0	0	0.7
Total acidics	1.5	1.4	1.1
NO	0	0	0
NO_2 and CO_2	1.5	1.4	1.1
CO	0.4	1.2	0
Combustibles	0.6	2.9	2.5
N_2O	63.7	58.8	58.3
Nitrogen	14.7	26.4	33.0

Haleite: Same as above except temp. of test was 130°C.

	Gas sample taken at	
	6 days	8 days
Oxygen	0%	0%
Moisture (Note 1)	8.6	4.9
Basics	0	0
Total acidics	1.5	1.7
NO	1.5	1.7
CO_2 and NO_2	0	0
CO	1.8	4.8
Combustibles	0	0
N_2O	63.3	59.4
Nitrogen	23.3	29.2

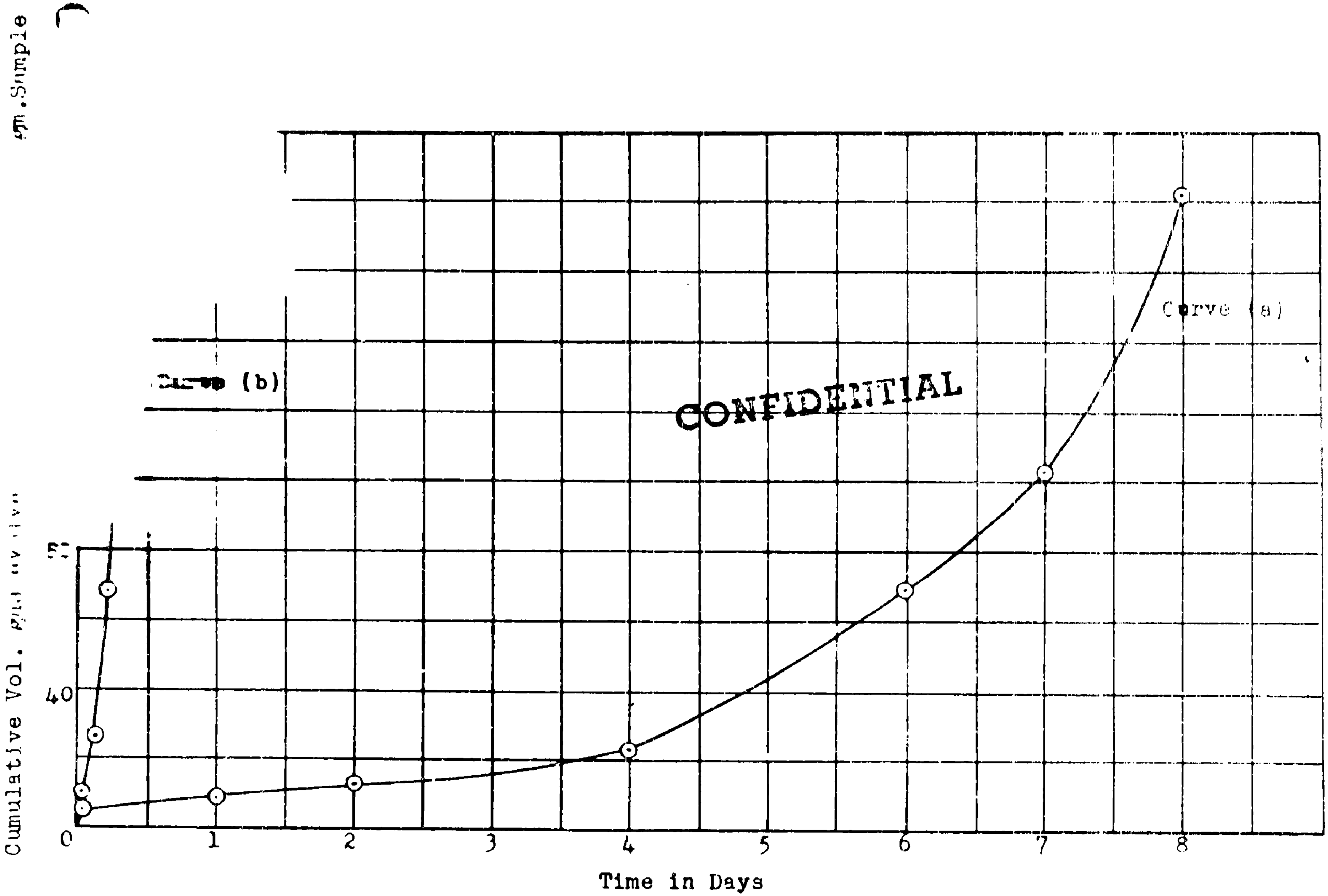
Note 1. Under this heading is included a substance removed by either a KOH or P_2O_5 bead which gives a brown coating on the bead.

Other work has been done on filling in data and checking results on PETN and Pentolite incidental to the preparation of a formal report.



Cumulative Vol. gas evolved in NTP cc. equiv. to 5.0gm.Sample
125
75
50
25
0
1
2
3
4
5
6
7
Time In Hours
CONFIDENTIAL

Figure 1



gm. Sample
Cumulative Vol.
40
0
1
2
3
4
5
6
7
8
Curve (a)
Curve (b)
CONFIDENTIAL
Time in Days

Figure 2

CONTROLLED DECOMPOSITION OF NITROCELLULOSE

Report Submitted by
R. C. Elderfield
Columbia University

HCl Decomposition Studies on the White Substance (WS)

In the previous report the results of preliminary experiments on the distillation of WS with 12% HCl were mentioned. A continuation of this work has shown that when heated with 12-13% HCl, WS first evolves CO_2, then a volatile carbonyl compound, and finally furfural. The non-volatile residue contains levulinic and oxalic acids.

Products from the Distillate

2.0 g. of WS (13A-71-26) was heated with 50 cc. of 13% HCl and the exit gases passed through a train containing saturated barium hydroxide solution. After CO_2 evolution had ceased, the system was swept out with CO_2 free air and the precipitated barium carbonate collected, dried, and weighed. The 1.40 g. of precipitate found corresponds to 0.31 g. of CO_2 or 15-1/2% of the original weight of WS. A repeat experiment gave 13-1/2% CO_2.

1.0 g. of WS (7A-56-24) was distilled with 25 cc. of 13% HCl, water being added intermittently to keep the HCl at approximately the original concentration. The distillate was collected under a cold saturated solution of 2,4-dinitrophenylhydrazine in dilute HCl. The latter became cloudy after the first few drops of distillate came over, and a precipitate formed on standing. The precipitation was not due to the CO_2 evolved. Two recrystallizations of the precipitate from dilute ethanol gave lemon yellow needles, m.p. 63-64°C. The latter was not soluble in dilute sodium hydroxide. Analyses are in progress.

The WS - HCl distillation was continued until the solution being distilled began to change in color from lemon yellow to reddish brown, at which time the WS had almost completely dissolved. Up to this point the distillate gave a negative aniline acetate test for furfural.

A fresh sample of dinitrophenylhydrazine was then placed in the receiver and distillation continued. Whereas the first precipitate formed had been yellow, the distillate now coming over gave an orange red precipitate. Two recrystallization from dilute ethanol gave a dark red solid melting at 182-184°C.

Mixed with synthetic furfural-2,4-dinitrophenylhydrazone, it melted at 183-185°C. Huntress-Mulliken (Identification of Pure Organic Compounds, 58 (1941)) gives ca. 185°C. as the m.p. of mixtures of the yellow and red forms of the derivative.

2.0 g. of WS was distilled with 50 cc. of 13% HCl at 30-35°C. and 15 mm. pressure. Copious CO_2 evolution occurred, but the decomposition of WS was much slower than when the distillation was carried out at atmospheric pressure as indicated by the fact that 1.03 g. of WS remained undissolved after 30 cc. of solution had distilled over.

The distillate gave a negative aniline acetate test for furfural, gave no precipitate with barium hydroxide, but did give a precipitate with 2,4-dinitrophenylhydrazine. These observations point to the presence of the above mentioned non-acidic volatile carbonyl compound.

The WS which remained undissolved had about the same base solubility as the original WS, indicating that decarboxylation probably occurs simultaneously with the decomposition of the WS into water soluble components.

Products from the Residual Solution

The residues from several WS - HCl distillations were charcoaled and neutralized with NaOH. After evaporation to dryness under reduced pressure, 50 cc. of ethanol and 1 cc. of con. sulfuric acid were added and the whole refluxed for 4 hours.

After filtration from the precipitated salts, the alcohol solution was concentrated under vacuum, 10 cc. of water added, and the solution again charcoaled. To 2 cc. portions at the lemon yellow filtrate were added 3 drops of phenylhydrazine in dilute acetic acid. The solution immediately became cloudy, and precipitation occurred on standing. Two recrystallizations from dilute ethanol gave buff-white crystals melting at 103-106°C. Mixed with synthetic ethyl levulinate phenylhydrazone, they melted at 104-106°C.

When a dilute calcium acetate solution was added to a sample of the charcoaled WS - HCl distillation residues, the latter immediately became cloudy, and formed a precipitate on standing overnight. The precipitate rapidly reduced warm dilute acid permanganate. This was taken to indicate oxalic acid, although the latter has not been confirmed further.

Tests on the Red Substance (RS)

Our RS has an odor (other than that due to oxides of N) very similar to that of levulinic acid, and since the latter was found as a WS - HCl decomposition product, it was sought (but has not as yet been identified) in RS.

10 cc. of RS (7A-56-26), previously concentrated in vacuo over sulfuric acid, was refluxed for 4 hours with 50 cc. of ethanol and 0.5 cc. of con. sulfuric acid. The dark red solution was neutralized with sodium bicarbonate, filtered, and excess solvent and other volatiles removed under vacuum.

The residual liquid (10 cc.) was diluted to 50 cc. with water, charcoaled and filtered. The light yellow filtrate gave an immediate precipitate with phenylhydrazine in dilute acetic acid. This yellow-orange precipitate, after six recrystallizations from dilute ethanol, melted sharply at 165-6°C., recalling the slightly lower melting phenylhydrazones (10A-63-26 and 21B-92-13) previously isolated from RS. An attempted preparation of the semicarbazone gave an almost white product melting above 240°C. The phenylhydrazone of glyoxal is reported to melt at 169-170°C. (values to 180°C. are also given) while its semicarbazone melts at 270°C. Since ethyl levulinate (b.p. 205°C.) rather than glyoxal (b.p. 50°C.) was being sought, a considerable amount of the latter may have volatilized during concentration of the solution in vacuo. In connection with the above see the last monthly report of M. L. Wolfrom (PT-18, page 54 ff.)

Work on the problem to date tends to favor the view that WS is essentially a nitric acid ester of a polyglucuronic acid. Additional evidence for or against this hypothesis is being investigated.

Decomposition of the White Substance by Water Alone

Work has been continued on an examination of the products obtained on decomposition of WS on boiling with water without the addition of HCl. The evidence previously presented for the formation of oxalic acid under these circumstances has been confirmed. Last month a crystalline cadmium salt was obtained which furnished analytical figures approximating those of cadmium oxalate. This cadmium salt has now been converted to calcium oxalate, which has been identified by permanganate titration and by the isolation of pure oxalic acid from it.

In the last monthly report it was suggested that oxalic acid itself might be a constituent of WS rather than a decomposition product of it. This view has now been definitely disproved. An aqueous extract of WS was prepared by dissolving WS in the minimum amount of alcohol and pouring this solution into water. The resulting suspension was filtered from insoluble material and the process repeated three times at the end of which 75% of the WS was in solution. This solution was then concentrated under reduced pressure with the temperature never rising above 30°C. After making the concentrated solution ammoniacal, calcium hydroxide solution was added, but no precipitate of calcium oxalate was found. We therefore conclude that oxalic acid is formed from WS only on heating with water and is to be considered a decomposition product of the material.

When ammonium hydroxide is added to an aqueous solution of WS prepared as above, there is immediate darkening of the solution and some tarry material separates. After filtration of the tarry material, the dark colored filtrate was allowed to evaporate at room temperature during which a partly crystalline precipitate, presumably of an ammonium salt, separated. Attempts to purify this and free it from contaminating tar have not been particularly successful. Efforts along this line are being continued.

CONTROLLED DECOMPOSITION OF NITROCELLULOSE

Report Submitted by
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Summary

Analyses are reported for formaldehyde, glyoxal, formic acid, acetic acid, ethyl acetate and water on RS from sheets of NC, both 12.6% N and 13.4% N, treated with nickel and untreated.

Material.

Sheets of Nitrocellulose, both 12.6% N and 13.4% N, containing nickel were prepared according to a procedure obtained from Captain Frazer, Aberdeen (letter dated January 31, 1944). Samples of RS were then prepared in the usual manner.

Experimental.

1. The Preparation of NC Sheets Containing Nickel.

Sheets of nitrocellulose impregnated with nickel were prepared by a procedure obtained from Captain J. H. Frazer,[2] Aberdeen.

An accurate estimation of the water content of the nitrocellulose (NC) was made by determining the loss of weight when the NC was dried in a vacuum oven at 60°C.

A quantity of the moist NC was suspended in 2 liters of distilled water in a 4-liter beaker equipped with a mechanical stirrer and the slurry stirred for thirty minutes. A solution of 0.5g. (0.0125 mole) of sodium hydroxide dissolved in 100 ml of water was added. After stirring for ten minutes, a solution of 3.42 g (0.013 mole) of nickel sulfate hexahydrate ($NiSO_4.6H_2O$) dissolved in 200 ml of water was added and the slurry stirred for an additional thirty minutes. The mixture was then washed four times with water by decantation, filtered, dehydrated with absolute ethanol and dissolved in ethyl acetate in the usual manner. Sheets of NC thus prepared possessed a very faint green color.

2. Estimation of Nitrous Acid in the Presence of Nitrates.

Using the method of Miller[1] a sample of (ca. 0.2 g.) freshly prepared trap RS was diluted to 50 ml. and mixed with three drops of dimethyl aniline reagent (8 g. dimethyl aniline and 9 ml. concentrated hydrochloric acid diluted to 100 ml.) and one drop of concentrated hydrochloric acid. After standing for thirty minutes, the yellow color of the RS solution was compared with a standard of sodium nitrite treated in the same manner. The content of nitrous acid was estimated to be less than 0.1% in RS. Older samples of RS (one to four weeks at 4°C.) gave negative tests for nitrous acid.

3. Determination of CH_3-C Groups (Acetic Acid, Ethanol, Ethyl Acetate)

Using the procedure of Kuhn and Roth[3] a sample of RS was analyzed for CH_3-C groups.

A 500-ml. three-necked, round-bottomed flask was provided with a reflux condenser, dropping funnel and a tube extending nearly to the bottom of the flask for introducing dry air. The air was passed through concentrated sulfuric acid (to which a little chromic anhydride was added), 40% sodium hydroxide and dry soda lime.

A weighed quantity of RS (ca. 1 g.) was placed in the flask and 100 ml. of chromic acid solution (16.8 g. of chromic oxide, 80 ml. concentrated sulfuric acid and 20 ml. of water) was added slowly from the dropping funnel. At the end of the addition the reaction mixture was refluxed gently for two hours. A stream of dry air was slowly passed through the mixture to prevent bumping and to sweep out any carbon dioxide formed. The mixture was then cooled and hydrazine hydrate (50% aqueous solution was added very cautiously until a green tinge appeared. The mixture was neutralized with 40% sodium hydroxide followed by acidification with 85% phosphoric acid.

The mixture was then steam distilled at constant volume and the CH_3-C groups determined as acetic acid by titrating the distillate with standard base.

4. Determination of Ethanol by Potassium Dichromate Oxidation.[4]

The steam distillate of neutralized RS (ca. 0.2 g.), 25 ml. of a 0.2 N potassium dichromate and 4.5 ml. of dilute sulfuric acid (1:5) were placed in a citrate of magnesia bottle and tightly stoppered. The bottle was heated by steam for six hours, cooled, and transferred to an iodine flask. A 2% solution of potassium iodide were added and allowed to stand for thirty minutes. The iodine was titrated with 0.1 N sodium thiosulfate. A blank determination was run.

D. Conclusions.

It is to be noted (Table III) that glyoxal and formic acid are present in approximately equimolar amounts, together with very significantly smaller molar amounts of formaldehyde and larger molar amounts of water.

The nitrocellulose of 13.4% nitrogen content produces a smaller amount of intermediate decomposition products than the nitrocellulose of lower nitrogen content (12.5%)(Tables I and II). Thus, the former has proceeded further toward the stage of complete decomposition.

When nickel is incorporated in the nitrocellulose of lower nitrogen content (12.6%), the yields of intermediate decomposition products show a trend toward lower values (Tables II and III). This effect is not strongly marked but would appear to be real. Therefore the nickel would appear to promote more complete decomposition of the nitrocellulose.

The determination of CH_3-C groups in RS were carried out by the of Kuhn and Roth[3] to determine the amount of ethanol present in RS. The method is not quantitative in this application. However, when considered in light of the determination of ethyl acetate by saponification and the determination of acetic acid by distillation, it is evident that there is not an appreciable amount of ethanol present. Approximately 89% of the CH_3-C groups determined as ethyl acetate and acetic acid were found by the Kuhn-Roth method.

The oxidation of the steam distillate of neutralized RS by the method of Poznanski[4], which would convert the free ethanol and that combined as ethyl acetate to acetic acid, was not quantitative. The amount of potassium dichromate consumed corresponded to 80% of the ethanol present as ehtyl acetate.

Freshly prepared trap RS gave weak tests[1] for nitrous acid (less than 0.1%).

It seems apparent from our work that the significant components of RS are formaldehyde, glyoxal, formic acid and water.

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References

1. E. Holl Miller, Analyst, 37, 345 (1912).
2. Communication, Capt. J.H. Frazer, Aberdeen January 31, 1944.
3. R. Kuhn and H. Roth, Ber., 66, 1274 (1933).
4. S. Poznanski, J. Am. Chem. Soc., 50, 981 (1928).

Table I

Typical Yields in Grams of RS from 100 g of NC

	12.6% N			13.4% N		
	Acetone Sheet	Ethyl Acetate Sheet	Nickel Catalyst Ethyl Acetate	Acetone Sheet	Acetate Sheet	Nickel Catalyst Ethyl Acetate
Tube		24.9	26.7	17.8	11.5	22.2
Trap	16.0	16.0	17.5	18.5	15.6	15.8
Total		40.9	44.2	36.3	27.1	38.0

Table II

Distribution of RS in Tube and Trap. Recorded as millimols per gram of NC

	12.6% N Ethyl acetate sheet				13.4% N Ethyl acetate sheet			
	Plain		Nickel catalyst		Plain		Nickel catalyst	
	Tube	Trap	Tube	Trap	Tube	Trap	Tube	Trap
Glyoxal	1.32	0.22	1.03	0.19	0.62	0.19	0.90	0.14
Formaldehyde	0.56	0.01	0.68	0.00	0.46	0.05	0.57	0.00
Formic acid	1.19	0.98	1.05	0.51	0.65	0.88	0.79	0.51
Water	1.80	1.90	1.19	1.26	1.42	2.55	1.45	1.80

Table III

Components of RS Recorded as Millimoles (tube and trap combined) Per Gram of Nitrocellulose

	12.6% N Ethyl acetate sheet		13.4% N Ethyl acetate sheet	
	Plain	Nickel Catalyst	Plain	Nickel catalyst
Formic acid	2.17	1.54	1.55	1.47
Water	3.70	2.45	3.95	3.11
Glyoxal	1.55	1.22	0.81	0.96
Formaldehyde	0.56	0.68	0.50	0.57

Table IV

Percentage Composition by Weight of RS

	12.6% N				13.4% N			
	EtOAc sheet untreated		EtOAc sheet Ni catalyst		EtOAc sheet untreated		EtOAc sheet Ni catalyst	
	Tube	Trap	Tube	Trap	Tube	Trap	Tube	Trap
Formaldehyde	6.7	0.24	7.6	0	10.2	5.5	7.6	0
Glyoxal	30.2	7.6	22.5	6.3	25.0	6.7	23.3	5.2
Formic acid	22.0	27.2	17.4	13.4	20.7	17.7	16.4	14.8
Acetic acid	1.4	11.9	1.1	21.2	4.2	9.5	3.2	17.6
Water	12.9	20.7	8.5	12.9	11.6	21.5	11.5	20.5
Ethyl acetate	3.5	16.6	-	-	-	-	-	-
Nitric acid	-	ca.1.0	-	-	-	-	-	-
Nitrous acid	-	<0.1	-	-	-	-	-	-
Total	76.7	85.34	57.1	53.8	71.7	60.9	62.0	58.1

STUDIES RELATING TO THE PREPARATION AND PROPERTIES OF MeNENA

Report Submitted By

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Summary

1. MeNENA was prepared very satisfactorily on a larger scale than heretofore. No disadvantages in a large scale batch process seemed apparent.

2. The solubility of MeNENA in a solution corresponding to the diluted and neutralized mother liquor from procedure XXIV[1] was determined.

3. A film reactor for use in the preparation of MeNENA, DINA, and other nitroxyalkyl nitramines wherein the Bamberger reaction is employed is under construction. A preliminary description of the apparatus is given.

4. The preparations of N-(β-nitroxyethyl) ethylnitramine and N-(β-nitroxypropyl) methylnitramine which are related to MeNENA and NENA are described.

Discussion

Experiments on the Preparation of MeNENA

The preparation of MeNENA on a larger scale than carried out previously disclosed no difficulty of operation and gave 86.9 percent yields of MeNENA (three mole run).

The preparation of the amine-nitric acid solution by the concurrent and simultaneous addition of the amine and nitric acid to an amine-nitric acid solution was found to be very advantageous in controlling the temperature of the first step of the reaction.

Solubility Data on MeNENA

The solubility of MeNENA in a solution corresponding to the diluted and neutralized mother liquor from Procedure XXIV[2] was

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1. Division 8 Interim Report PT-18, page 78 ff.)

2. PT-18, page 78 ff.

determined. The solution contains theoretically 2.2 moles of sodium acetate and 0.05 moles of sodium nitrate in 550 cc. of water after neutralization with sodium carbonate. This corresponds to concentrations of 0.4 moles of sodium acetate and 0.009 moles of sodium nitrate in 100 cc. of water. The solubility of MeNENA in this solution was determined by adding a weighed amount of MeNENA and filtering off the undissolved material after shaking for twenty hours at room temperature. The solubility was found to be 0.088 g. of MeNENA per 100 cc. of water. For Procedure XXIV this corresponds to a loss of product of 0.48 g. of MeNENA or 0.6 per cent of the theoretical yield.

Design of Apparatus for a Continuous Process for MeNENA and Related Compounds.

A film reactor is under construction. This consists of a 3-inch diameter, 4-foot long Pyrex tube which will be mounted on inclined motor driven rollers. Continuous feeds at the upper end of the tube will maintain a continuous film of reacting material on the inside surface of the tube. The material will flow down the tube due to the incline and will flow out the end and be quenched in a receiver containing ice and water.

Further details of construction and operation will be reported when the apparatus has been put into actual use.

Other Derivatives of NENA

The synthesis of N-(β-nitroxyethyl) nitramine (NENA)[3] has been reported and the synthesis of N-(β-nitroxyethyl) methylnitramine (MeNENA)[4] has been described and the explosive properties of these compounds ascertained.

The preparation of two derivatives related to NENA and MeNENA has been carried out for the purpose of obtaining data on their explosive properties. These are N-(β-nitroxyethyl) ethylnitramine (EtNENA) and N-(β-nitroxypropyl) methylnitramine (Me_2NENA). Both of these nitroxyalkyl nitramines are obtainable from the corresponding alkamine dinitrate, acetic anhydride and a chloride catalyst.

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[3] PT-17, page 65.

[4] Division 8 Interim Report PT-17, page 65 ff.; PT-18, page 64 ff.

The preparation of EtNENA was carried out according to the following:

$$C_2H_5\text{-}NH\text{-}CH_2CH_2OH \xrightarrow{HNO_3} C_2H_5\text{-}\overset{+}{N}H_2\text{-}CH_2CH_2ONO_2 \quad NO_3^-$$

$$\underset{NO_3^-}{C_2H_5\text{-}NH_2^+\text{-}CH_2CH_2ONO_2} \xrightarrow[Cl^-]{Ac_2O} C_2H_5\text{-}\underset{NO_2}{\underset{|}{N}}\text{-}CH_2CH_2ONO_2$$

Me_2NENA was prepared as follows:

$$CH_3\text{-}NH\text{-}CH_2CHOHCH_3 \xrightarrow{HNO_3} \underset{NO_3^-}{CH_3\text{-}NH_2^+}\text{-}CH_2\underset{ONO_2}{\underset{|}{C}}HCH_3$$

$$\underset{NO_3^-}{CH_3\text{-}NH_2^+}\text{-}CH_2\underset{ONO_2}{C}HCH_3 \xrightarrow[Cl^-]{Ac_2O} CH_3\text{-}\underset{NO_2}{\underset{|}{N}}\text{-}CH_2\text{-}\underset{ONO_2}{\underset{|}{CH}}\text{-}CH_3$$

EXPERIMENTAL PART

Preparation of MeNENA

Into a one-liter four-necked flask provided with stirrer, thermometer, and two dropping there was placed a solution consisting of 37.5 g. (0.5 mole) methyl ethanolamine and 67.7 g. (1.05 mole) of 98 per cent nitric acid. This mixture was prepared as described in Procedure XXIV[5]. There was then added concurrently and simultaneously 18.75 g. (2.5 moles) of methyl ethanolamine and 338.5 g. (5.25 moles) of 98 per cent nitric acid. The temperature throughout the addition was kept at 10-15°C.

The three mole mixture of alkamine dinitrate was transferred to a dropping funnel and added to a solution of 708 g. (6.6 moles) of acetic anhydride and 5.2 g. (0.066 mole) of acetyl chloride contained in a three -liter flask. Moderate stirring was employed and the reaction maintained at 35°C. The addition required twenty minutes. After the addition the reaction was

[5] PT-18, page 78 ff.

stirred for fifteen minutes at the same temperature and then poured over 3300 cc. of ice and water. MeNENA precipitated and was filtered and washed with three 300 cc. portions of water. There was obtained 416 g. of the substance, melting at 37-38°C.

The filtrate containing the washings was neutralized with a calculated amount of sodium carbonate. Approximately 20 g. of additional product was obtained. This was recrystallized from ether and there was obtained 14 g. of second crop MeNENA, m.p. 38-39°C.

Total Yield: 86.9 per cent.

Preparation of EtNENA

Into a 500 cc. three-necked flask containing 67.7 g. (1.05 moles) of 98 per cent nitric acid and equipped with stirrer, thermometer, and a capillary-tipped dropping funnel whose end was immersed below the surface of the acid, there was added 44.5 g. (0.5 mole) of ethyl ethanolamine. The contents of the flask was cooled externally and the temperature maintained below 10°C. during the addition.

The amine-nitric acid mixture was transferred to a dropping funnel and added dropwise to a solution of 118 g. (1.1 moles) of 95 per cent acetic anhydride and 0.86 g. (0.011 mole) of acetyl chloride contained in a 500 cc., three-necked flask. Moderate stirring was employed and the reaction was maintained at 35°C. After the addition of the amine-nitric acid mixture which required fifteen minutes, the reaction was kept at 35°C. for an additional fifteen minutes. After pouring the contents of the flask into 550 cc. of ice and water there was obtained an oil which was separated and washed successively with two 100 cc. portions of 5 per cent sodium bicarbonate and two 100 cc. portions of water. After filtering, the pale yellow oil was dried by bubbling dry air through it. There was obtained 73.4 g. (82 per cent of theoretical) of N-(β nitroxyethyl ethylnitramine melting at 4-5.5°C.

$D_4^{25} = 1.32$; $n_D^{25} = 1.479$.
Theoretical molecular refraction = 38.75.
Observed molecular refraction = 38.4.

Preparation of Me$_2$NENA

The preparation of Me$_2$NENA, N-(β-nitroxypropyl) methylnitramine, was carried out paralleling the directions for the proparation of EtNENA, using as the starting material methyl isopropanolamine.

From 44.5 g. (0.5 mole) of the amine there was obtained 65.8 g. (74 per cent of theoretical) of N-(β-nitroxypropyl) methylnitramine as a pale yellow oil, melting at 22-23°C.

$$D_4^{25} = 1.32; \; n_D^{25} = 1.478.$$

Theoretical molecular refraction = 38.75.
Observed molecular refraction = 38.5.

STUDIES OF NITRAMINES

Report Submitted by
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Summary

A study of the nitration of sym. diphenyl guanidine was begun. It is desired to obtain the hexanitro-derivative and higher derivatives in sufficient quantity for testing.

Several nitrated intermediates have been obtained but their structure is uncertain because no analyses have been made.

Experimental

Nitration by acetic anhydride and 98% nitric acid at 0°C.

To 20 cc. of 98% HNO_3 cooled to 10° was added with stirring 20 cc. of acetic anhydride containing a few drops of acetyl chloride. The mixture was cooled to 0°C and 5.3 g. (0.025 moles) of diphenyl guanidine was added portion-wise with stirring. The addition took 1 1/4 hours. It was stirred 1/2 hours longer and then poured into an ice-water mixture. The solid yellow product was washed with ice H_2O, filtered, dried, and weighed 7.0 g. (The product just after filtering seemed to hold a great deal of water which seemed to effloresce.) The crude product melted between 80° - 90°C and burned very fast leaving a black ash. It is soluble in hot acetone, hot water, hot 95% ethanol, and hot ethyl acetate but only slightly soluble in ether and benzene. It was recrystallized from ethyl acetate by evaporation giving yellow crystals that melted 157-159°C with foaming and decomposed at 175-180°C. It burned very fast in the open flame.

Nitration with 98% nitric acid and con. sulfuric acid at 0°C.

To a mixture of 8.5 cc. of 98% HNO_3 and 21.9 cc. of con. H_2SO_4 was added 2.0 g. (0.011 moles) of diphenyl guanidine at 0°C with stirring. After the addition the solution was kept at 0°C. 1/2 hour longer, then poured into ice and water. The yellow solid that precipitated was washed a few times with ice water and then dried in the air. It weighed 4.5 g. It melted 182°-184°C with decomposition when recrystallized by evaporation from ethyl acetate. In an open flame it burned the same as the product obtained above.

Nitration with mixed acid at higher temperature.

A solution of 5 g. (0.024 moles) of diphenyl guanidine in 12 cc. of con. sulfuric acid was added dropwise over a 2 hour period to 15 cc. of fuming nitric acid at 35° - 40°C with constant stirring. After the addition, the stirring is continued 1/2 hour, then the solution was slowly heated to 60°C and left standing at room temperature overnight. It was then treated with ice and water giving a yellow solid which filtered and dried. It weighed 7.g. and melted after crystallization from ethyl acetate, 182°-185°C.

To a mixture of 4 cc. of conc. sulfuric acid and 8cc. of fuming nitric acid was added 5 g. of the above crude product. The suspension was heated on a steam bath for 1 hour with constant stirring, then treated with ice and water. The dried product weighed 5 g. It was crystallized from ethyl acetate giving two crops of yellow crystals that melted at 176°-178°C. and 196°-200°C. with decomposition. In an open flame the higher melting material burns faster and more completely.

POLAROGRAPHIC INVESTIGATION OF EXPLOSIVES

Report Submitted by
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Polarographic Investigation of Antimonous Sulfide

In our previous report (PT-18, page 85 ff.) it was pointed out that Sb_2S_3 can be dissolved in a hot solution that is 4 M in potassium tartrate. After diluting fourfold the solution yields a polarogram that comprises a fairly well defined anodic sulfide wave and a poorly defined cathodic antimony wave. It was pointed out that antimony and sulfide each have a deleterious effect on the definition of the wave of the other. Furthermore it was shown that addition of + 3 antimony to a sulfide solution decreases the diffusion current of the sulfide to a marked extent.

To determine if the diffusion current of sulfide ion is directly proportional to the concentration of sulfide when the ratio of the concentrations of antimony and sulfide is kept constant, numerous experiments were performed in which various amounts of antimony sulfide were dissolved in the alkaline tartrate solution and the anodic sulfide diffusion current was measured. Although a fair proportionality was obtained between the weight of Sb_2S_3 taken and the magnitude of the sulfide wave, several difficulties arose and erratic results were obtained frequently. Most of the difficulties were later traced to air oxidation of the sulfide ion during the solution of the antimony sulfide, which dictates that oxygen (air) must be excluded during the solution process.

It was also noted that solutions of Sb_2S_3 in the alkaline tartrate medium slowly deposit a dark precipitate after standing for a few hours. Polarographic analysis of this precipitate showed that it contained antimony.

Because of these complications we have decided to abandon attempts to determine sulfide directly from the polarogram of the alkaline tartrate solution of Sb_2S_3, and have begun experiments in which the sulfide will be separated from the antimony prior to its polarographic determination. In the method now being developed samples of Sb_2S_3 are dissolved by boiling with the alkaline tartrate solution under reflux and in an atmosphere of nitrogen. When solution of the sample is complete, an excess of hydrochloric acid is added, the solution is boiled gently, and the hydrogen sulfide is swept out with nitrogen and absorbed in a solution of sodium hydroxide. The receiving solution is then made up to known volume and the anodic sulfide wave is recorded. The hydrogen sulfide is swept out through a reflux condenser to prevent loss of antimony chloride from the acidified solution.

The antimony is determined by diluting the residual solution to known volume in 1 N hydrochloric acid, and recording a polarogram of this solution.

Preliminary results indicate that this procedure will lead to satisfactory determinations of both sulfide and antimony, and that it will be applicable to relatively small quantities of sample. A complete description of the apparatus and analytical procedure will be given in next month's report.

Tentative Plan of Analysis of Primers

Sufficient information about the polarographic characteristics of the chief components of primers has now been obtained to justify starting on the analysis of typical primer mixtures. Provision is being made for the possible presence of mercuric fulminate, lead azide, and antimonous sulfide, mixed with charcoal, sulfur, potassium chlorate, etc.

It is planned first to extract the sample with an ammonium acetate solution, which will dissolve lead azide, mercuric fulminate, potassium chlorate, and other water-soluble salts. After acidifying this solution with hydrochloric acid the mercury and lead can be determined simultaneously from a single polarogram.

Experiments have shown that Sb_2S_3 is sufficiently in ammonium acetate solution to remain quantitatively in the residue for the first extraction, and hence it is planned to determine sulfide and antimony in this residue as described above.

If lead thiocyanate and/or lead styphnate are present in the sample they will both dissolve in the ammonium acetate extract, and should thus be determinable without much difficulty.

It may also be possible to determine azide in the ammonium acetate extract from its anodic wave with the platinum microelectrode (See PT-18), provided that conditions can be arranged to avoid its decomposition.

Since thiocyanate ion produces an anodic wave with the dropping electrode we expect that it may also be possible to determine thiocyanate in the ammonium acetate extract.

Cuprous thiocyanate is also frequently present in primers and provision for its determination will also have to be made. By performing the extraction with ammonium acetate in a nitrogen atmosphere to avoid oxidation of the cuprous copper, the cuprous thiocyanate will probably remain quantitatively insoluble and probably can be determined along with the antimony.

Sulfur will not be determinable polarographically, but it should not interfere with the other determinations.

As soon as the method of determining Sb_2S_3 has been worked out, experiments will be started with synthetic primer mixtures containing all of these substances.

POLAROGRAPHIC EXAMINATION OF EXPLOSIVES

Report Submitted by
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University of Wisconsin

I. Additional information on diphenylamine:

In our last report (PT-18, page 92 ff.) introductory information about the action of diphenylamine as a stabilizer for nitrocellulose was given. We reported the outline showing the transformations of diphenylamine as given by Davis and Ashdown (1). A later reference gives a more complete picture of the changes occurring. Becker and Hunold (2) give the following series:

1. diphenylamine
2. diphenylnitrosoamine
3. 2- and 4-mononitrodiphenylamine
4. 2- and 4-mononitrodiphenylnitrosoamine
5. 2,4'- and 4,4'-dinitrodiphenylamine
6. 2,4'- and 4,4'-dinitrodiphenylnitrosoamine
7. 2,4,4'-trinitrodiphenylamine

These compounds were detected by color reactions in powder which had been heated at 100°C.; 2. (above) detected before heating started; 3. after heating one day; 5. after heating three days; and 7. after heating four days. This presents a more complicated picture than that described by Davis and Ashdown.

II. Change of solvent for the system.

In the last report we indicated that our present work was to be done in 90 per cent alcoholic solutions. Nitration products of diphenylamine have only limited solubility in such a system. In the examination of other solvent+water systems, it was found that dioxane-water combinations with as high as 50 per cent water gave good results. At present we have not obtained all of the products from the above series that we need. For this reason we used 80 per cent dioxane. This ought to provide a sufficient margin of solubility so that no change will be necessary when we begin work with other compounds of the series. One disadvantage of using a system of this composition is that one is limited in the number of supporting electrolytes which are usable. Lithium hydroxide, sodium hydroxide, potassium hydroxide, lithium chloride, sodium chloride, potassium chloride and ammonium chloride were found to be of limited use because of the tendency to promite the formation of two layers in the dioxane-water

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1. Davis and Ashdown, Ind. Eng. Chem. 17, 674, (1925)
2. Becker and Hunold, Z.ges.Schiess u. Sprengstoffw., 33, 213, (1938) and 33, 244, (1938)

system. Herz and Lorentz (3) give the solubilities of some additional salts and organic acids in dioxane-water systems, along with useful information on density, viscosity and surface tension measurements.

Mention should be made of precautions in the use of commercial dioxane. The usual product frequently contains small amounts of glycol acetal and water. After standing, the glycol acetal hydrolyzes and the liberated acetaldehyde gives rise to rapid peroxide formation. Purification and proper storage eliminate this danger and render the dioxane entirely satisfactory for polarographic purposes. Purification of the dioxane used in the present work is described below.

III. Materials.

Dioxane: Six liters of commercial dioxane, mixed with 85 ml of hydrochloric acid (SP.G. 1.175) and 600 ml of water, were refluxed for 18 hours while a slow stream of nitrogen was bubbled through the solution. This was cooled and potassium hydroxide was added until an excess was present and two layers had separated. The upper dioxane layer was decanted and the potassium hydroxide treatment repeated; contact with the potassium hydroxide pallets was continued for one hour, with occassional shaking. Dioxane was again decanted into a clean flask and refluxed with metallic sodium for eighteen hours, a very slow stream of nitrogen being passed through the solution during this period. The dioxane was then distilled from the sodium in the presence of nitrogen, collection of the distillate being made in the absence of air. The product was stored under an atmosphere of nitrogen. See references (4) and (5).

HCL --- reagent grade -- polarographically checked.
Ethyl alcohol -- purification in previous report.
Lithium chloride -- polarographically checked.
N-nitrosodiphenylamine -- synthesis and reference in PT-18.
p-nitrosodiphenylamine -- Eastman -- white label.
4-nitrodiphenylamine -- Eastman -- white label.

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(3) Herz and Lorentz, Z. physik.chem. Abt. A 140, 406, (1929)

(4) Hess and Frahm, Ber. 71B, 2627, (1938)

(5) Fieser, Exp. in Organic Chem. Part II, 368, (1941) Heath Publishers, 2nd Ed.

IV. N-Nitrosodiphenylamine.

(a) Acid solution in alcohol.

Table I

N-Nitrosodiphenylamine in 80% alcohol (by volume)
Supporting electrolyte 0.1 M HCl and 0.4 M LiCl
Mercury pressure - 58.3 cm
P/m -- 40.3
Drop time at 1/2 wave potential 3.3[illegible]
Hydrogen stream - 10 minutes

	mmols/liter	ma	i_d/c	
1.	0.5	3.27	6.[illegible]	1/2 wave -- 0.67
2.	1.0	6.72	6.72	
3.	1.5	10.68	7.12	$i_d/Cm^{2/3}t^{1/6} = 4.24$
4.	2.0	14.40	7.20	at 1 mmol
5.	2.5	17.94	7.18	

mean $i_d/c = 6.95$

(b) Alkaline solution in alcohol.

Table II

N-Nitrosodiphenylamine in 80% alcohol (by volume)
Supporting electrolyte 0.1 M NaOH and 0.25 M LiCl
Mercury pressure 58.3 cm
P/m -- 40.3
Drop time at half wave potential 3.[illegible]
Hydrogen stream - 10 minutes

	mmols/liter	ma	i_d/c	
1.	0.5	1.76	3.52	1/2 wave -- 1.17
2.	1.0	3.23	3.23	
3.	1.5	4.93	3.29	$i_d/Cm^{2/3}t^{1/6} = 2.03$
4.	2.0	6.66	3.33	at 1 mmol
5.**	2.5	8.31	3.32	

mean $i_d/c = 3.34$

** This curve shows a slight maximum

V. N-Nitrosodiphenylamine acid solution in dioxane.

Table III

N-Nitrosodiphenylamine
80% dioxane by volume
Supporting electrolyte 0.2 M HCl
Mercury pressure 58.3 cm
P/m -- 40.3
Drop time at half wave -- 3.85 sec

	mmols/liter	ma	i_d/c	
1.	0.5	3.72	7.44	1/2 wave = 0.67v
2.	1.0	7.32	7.32	
3.	1.5	11.07	7.38	$i_d/Cm^{2/3}t^{1/6} = 4.58$
4.	2.0	14.94	7.47	
5.	2.5	18.00	7.20	

mean $i_d/c = 7.34$

VI. P-Nitrosodiphenylamine in dioxane, acid solution.

Table IV

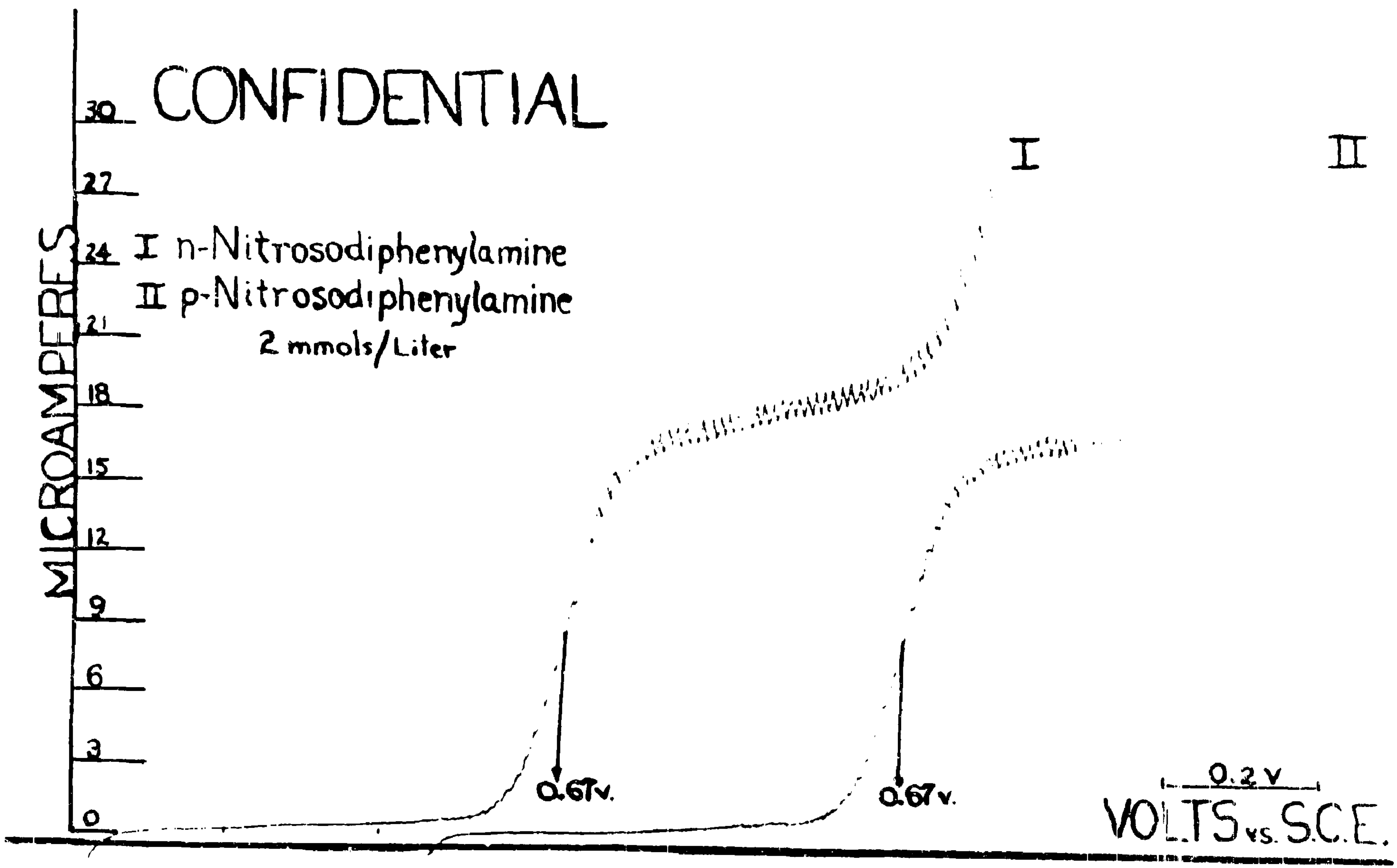
p-Nitrosodiphenylamine in 80% dioxane (by volume)
Supporting electrolyte 0.2 M HCl
Mercury pressure 58.3 cm
P/m -- 40.3
Drop time at half wave - 3.84

	mmols/liter	ma	i_d/c	
1.	0.5	3.57	7.14	
2.	1.0	7.32	7.32	1/2 wave = 0.67
3.	1.5	11.10	7.33	
4.	2.0	15.30	7.65	$i_d/Cm^{2/3}t^{1/6} = 4.62$
5.	2.5	18.90	7.66	

mean $i_d/c = 7.40$

VII. 4-Nitrodiphenylamine in dioxane in acid solution.

When this report was prepared, the curves for 4-nitrodiphenylamine showed a maximum of some prominence. We have only now succeeded in removing this maximum by the use of eosin. Data for the reduction will appear in the next progress report.



CONFIDENTIAL
I n-Nitrosodiphenylamine
II p-Nitrosodiphenylamine
2 mmols/Liter
MICROAMPERES
30
27
24
21
18
15
12
9
6
3
0
I
II
0.67v.
0.67v.
0.2 V
VOLTS vs. S.C.E.

Addition to data of last report.

In the curve for the reduction of n-nitrosodiphenylamine given in the last report, it should be mentioned that the first small wave is not a part of the reduction of the above named compound. The wave reported for the reduction indicates a simple one step process under the conditions described.

Conclusions.

From data available at the moment, it seems evident that the important products of nitration-oxidation of diphenylamine will be reducible at the dropping electrode. The fact that the 1/2 wave potential for p- and n-nitrosodiphenylamine is essentially the same will not interfere with our interpretation of state of preservation of the original powder. For this purpose it will not be necessary to differentiate between n- and p-nitrosodiphenylamine but rather to differentiate between the stages listed in Section I of this report.

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National Defense Research Committee, Office of Scientific Research and Development, Div. 8, Washington, D.C.
PREPARATION AND TESTING OF EXPLOSIVES, by Ralph Connor. Interim rept., 15 Feb-15 Mar 44. 71p illus, tbs. PT-19. [redacted]

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